Book Section:

North, Michael orcid.org/0000-0002-6668-5503 and Styring, Peter (2019) Introduction. In: North, Michael and Styring, Peter, (eds.) Carbon Dioxide Utilisation Volume 1. de Gruyter , pp. 3-12.

https://doi.org/10.1515/9783110563191

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1 Introduction

Welcome to *Carbon Dioxide Utilisation*: from fundamental discoveries to production processes. This book is aimed at advanced undergraduates and recent graduates studying carbon dioxide utilisation. Carbon dioxide utilisation is a highly interdisciplinary topic rooted not only in both chemistry and chemical engineering, but also impacting on physics, biological sciences and environmental science. This text assumes that the reader has a graduate-level knowledge of chemical sciences and in particular is familiar with chemical structures and thermodynamic concepts. Each chapter of this book has been written by one or more authors, at least one of whom is a member of CO2Chem. CO2Chem is a UK-based, global network of academics, industrialists and policy makers with an interest in carbon dioxide utilisation (CDU). It has over 1,000 members, covering not just the sciences but also social sciences such as sociology, economics and politics.

In planning this book we settled on the term carbon dioxide utilisation (often abbreviated as CDU) to most clearly describe the contents, but the topic is also often referred to as carbon capture and utilisation (CCU), which is related to carbon capture and storage (CCS). CDU refers to any technology that can take carbon dioxide and convert it into a more valuable chemical. Carbon dioxide is the end product of all combustion processes such as the burning of fossil fuels (Scheme 1.1) or biomass; it is produced as a by-product in many chemical processes [1] (Table 1.1) and it occurs naturally in the Earth's atmosphere. Prior to the industrial revolution, the concentration of carbon dioxide in the Earth's atmosphere was around 250 ppm, and by 2019 that had increased to over 410 ppm [2], mostly as a result of the global combustion of fossil fuels (coal, oil, gas) that provide the energy to support the lifestyle that we humans enjoy. It is now widely acknowledged that this increase in the atmospheric concentration of carbon dioxide is directly responsible for the global warming that has become apparent since the later decades of the twentieth century and for the associated climate changes that could make large parts of the currently inhabited regions of our planet unfit for human existence or for the production of food crops.

As Scheme 1.1 illustrates, not all fossil fuels produce the same amount of energy per mole of carbon dioxide emitted. Coal is the worst fuel in this respect, with liquid fuels (such as diesel, kerosene and petrol) next and natural gas producing almost twice as much energy per mole of carbon dioxide emitted as coal. Thus, by switching from coal to gas-fuelled power stations it is possible to significantly reduce the carbon dioxide emissions associated with electricity production. This is exactly the approach being taken by many countries (including the UK that has mandated that all coal burning power stations must close by 2025). Unfortunately, however, the known reserves of coal are far greater than those of oil and gas. The 2018 BP statistical review of world energy suggests that there is enough coal in known

https://doi.org/10.1515/9783110563191-001

Coal: $\underset{(s)}{C} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{CO_2}$ $\Delta H_r = -394$ kJ/mol

Petrol: $2\underset{(l)}{C_8H_{18}} + \underset{(g)}{25O_2} \longrightarrow \underset{(g)}{16CO_2} + \underset{(g)}{18H_2O}$ $\Delta H_r = -010, 160$ kJ/mol (−635 kJ/mol per CO_2 emitted)

Gas: $\underset{(g)}{CH_4} + \underset{(g)}{2O_2} \longrightarrow \underset{(g)}{CO_2} + \underset{(g)}{2H_2O}$ $\Delta H_r = -803$ kJ/mol

Scheme 1.1: Combustion of fossil fuels.

Table 1.1: Major sources of waste carbon dioxide.

Source	Global CO_2 emissions (10^6 t CO_2/year)	CO_2 purity (volume %)
Coal	14,200	12–15
Natural gas	6,320	3–5
Refineries	850	3–13
Cement production	2,000	14–33
Ethylene production	260	12
Iron and steel production	1,000	15
Natural gas production	50	5–70
Ammonia production	150	100

reserves to last for 134 years at the current rate of consumption, but known reserves of oil and gas will be consumed in 50–53 years at current consumption rates [3]. These figures are an oversimplification as new reserves of fossil fuels are being discovered, consumption is not constant (it has increased in all but one year since 1982 and is likely to keep doing so as the human population increases and becomes more affluent) and non-conventional reserves such as gas obtained by fracking are not included. However, the BP figures do illustrate the nature of the problem we face, and give an indication of the timescale: this is not a problem that can just be left for future generations; most readers of this book will expect to be alive in 50 years time! Scheme 1.1 also illustrates that combustion of any fossil fuel still produces carbon dioxide and whilst switching from coal to gas can roughly halve the carbon dioxide emissions associated with production of a fixed amount of electricity, this is not sufficient to meet the level of carbon dioxide emissions reduction required if we are to limit global warming and avoid the worst climate change effects as recommended by the United Nations International Committee on Climate Change.

Of course, there are ways of generating electricity that do not involve the combustion of fossil fuels. One option is to burn freshly grown biomass rather fossilised biomass. This is usually considered to be carbon neutral as the biomass has absorbed carbon dioxide from the atmosphere during its growth and this is simply returned to the atmosphere during its combustion. However, transportation of the biomass to the power station (which may be on a different continent) must be considered and the land use change needed to allow biomass burning on a global scale would be significant, resulting in competition for arable land between food and fuel crops. Other well-established electricity production methods do not involve combustion and so directly generate no carbon dioxide. Examples include nuclear and hydroelectric power schemes. However, both of these require large quantities of cement/concrete during their construction, and this results in carbon dioxide emissions (Table 1.1). Nuclear energy has its own safety and political problems and is also very expensive compared to the combustion of fossil fuels or biomass. Hydroelectric power generation involves significant land use change often associated with loss of habitat for possibly endangered species and loss of arable and habitable land. Over the last 10–20 years, there has been a significant shift in electricity generation towards the so-called renewable energy. This involves installations that can capture the energy from sunlight (photovoltaics), wind or wave power. Each individual renewable unit (wind turbine, photovoltaic cell, etc.) generates a tiny amount of electricity compared to the amounts needed globally or even nationally, but these technologies are easily scalable by numbers rather than by size. The effects can be dramatic; at one point in 2017, the UK produced over half its electricity from renewable sources. Throughout 2017, coal burning accounted for less than 7% of all UK electricity production and in 2018, the UK managed to generate all the electricity it needed for three consecutive days without burning any coal [4].

So in the long term, it should be possible to generate all the electricity needed for human activities from non-carbon dioxide-producing sources, but the pathway to get there will be a lengthy one. In addition, transportation fuel is difficult to decarbonise. Electric trains are already well established and electric cars are becoming more common, but the lithium ion battery technology used for electric cars is not viable for larger vehicles such as trucks or ships and air transport is another major unsolved problem. The scale of the air transport problem should not be underestimated. International aviation produces almost as much carbon dioxide as the whole of the UK emissions and more than a number of other countries including Australia, Italy and France [5]. Thus for the foreseeable future, human beings will continue to burn fossil fuels to generate at least some of the energy needed to support our civilisation. Furthermore, as Table 1.1 shows, many chemical processes that produce substances that are essential for modern life are also major producers of waste carbon dioxide. Thus, we could not construct towns and cities without iron, steel and cement and the ammonia produced is almost all used to prepare urea and ammonium nitrate that are used as fertilisers to grow the crops needed to support a population of 7.5 billion human beings. Given that the human population is predicted to reach 10 billion [6] as early as 2050 (just 31 years from the time this book was published), we will need to expand the production of these chemicals (and others) to cope with the 25% increase in the number of human beings on planet Earth.

The preceding paragraphs set the scene for the need for carbon dioxide utilisation. To be able to sustain (and further enhance) human lifestyle whilst coping with a rapidly increasing population, we need to keep generating waste carbon dioxide and to avoid the damaging effects of climate change this carbon dioxide cannot simply be dumped into the Earth's atmosphere. There are two technologies that have been proposed to allow this: carbon dioxide utilisation (i.e., carbon capture and utilisation) and carbon capture and storage. Carbon capture and storage involves capturing carbon dioxide (from point sources or the atmosphere), purifying and pressurising it, transporting the pressurised gas to suitable disposal site and then burying it underground or under water [7]. This is a very energy-intensive process; it has been estimated that for every three coal burning power stations that CCS is fitted too, a fourth power station of comparable specifications would be needed just to supply the energy needed to power the CCS units. Whilst this already seems highly undesirable, the switch from coal-fuelled power stations to gas-fuelled ones makes the situation even worse. The flue gas from a coal-burning power station contains 12–15% carbon dioxide whilst that produced from a gas-burning power station contains only 3–5% carbon dioxide. The reason for this difference can be seen in Scheme 1.1. For combustion of coal, carbon dioxide is (ideally) the only product, and so if all the oxygen was combusted, the flue gas would contain 80% nitrogen and 20% carbon dioxide. In reality, not all the oxygen is combusted to avoid forming highly poisonous carbon monoxide, and so the flue gas from a coal burning power station contains about 12–15% carbon dioxide. However, combustion of natural gas produces two water molecules (i.e. steam) for every carbon dioxide molecule and so the carbon dioxide concentration in the flue gas will be one-third that from burning coal, that is, 3–5%. The consequence of this is that whilst the carbon capture unit attached to a coal burning power station needs to concentrate the carbon dioxide six- to seven-fold, that attached to a gas burning power station would need to concentrate the carbon dioxide by about 20-fold. This requires far more energy to achieve.

One part of carbon capture and storage that is often overlooked is the transportation. This requires a pipeline from each carbon dioxide producer to the disposal site. Coal-fuelled power stations are much larger than gas-powered ones, and so fewer coal-burning power stations are needed. A typical coal-burning power station might produce 2GW of electricity, whilst a gas turbine-based power station typically produces just 50 MW. So around 40 gas-fuelled power stations would be needed to replace just one coal-burning power station. Coal-burning power stations are often located close to one another on coal fields to minimise the costs associated with transporting coal. Hence, a single pipeline could transport the carbon dioxide from multiple coal burning power stations. In contrast, gas is easily transported through the existing natural gas grids (western Europe already obtains gas in a pipeline that comes from Siberia), and so as coal burning-power stations are phased out and replaced with gas-fuelled ones, these are likely to be far more widely distributed in order to minimise the losses associated with transport of the electricity they produce. As a result, even if each gas-burning power station is fitted with a carbon capture unit, the transportation of the carbon dioxide to a storage site becomes prohibitively expensive.

The reader should also be aware of another issue with many proposed carbon capture and storage schemes. They are not really carbon capture and storage schemes at all, but rather enhanced oil recovery [8] schemes being passed off as carbon capture and storage. The difference is illustrated in Figure 1.1. Both processes involve capture and transport of waste carbon dioxide. Although carbon capture and storage transports the carbon dioxide to a storage site where it can simply be pumped underground or under water, enhanced oil recovery transports the carbon dioxide to a partly depleted oil field. The carbon dioxide is then pumped down an oil well to force more crude oil out of the well. This crude oil would not be recoverable by conventional means. The additional crude oil generated in this way is subsequently treated in the same way as any other crude oil, 95% of it will be converted into fuel and burned to produce more carbon dioxide. Clearly if more carbon dioxide is produced when this fuel is combusted than was originally pumped into the partly depleted oil well, then overall the enhanced oil recovery process will generate more carbon dioxide than it consumes and will be a dangerous pyramid scheme. The attractiveness of enhanced oil recovery is of course that it produces more oil and hence more profit for oil companies.

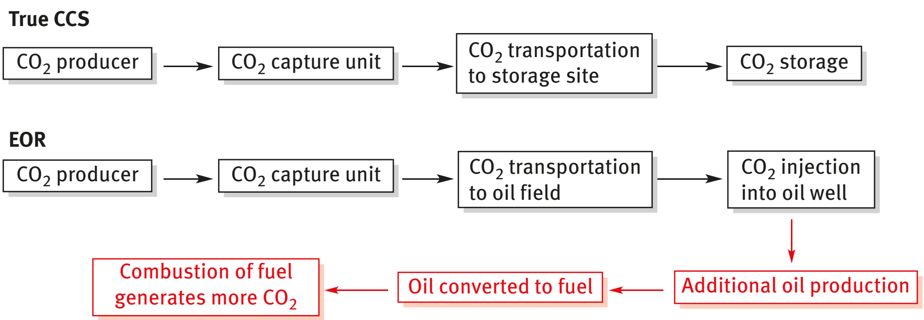


Figure 1.1: Comparative illustration of carbon capture and storage and enhanced oil recovery.

Another issue with carbon capture and storage that is apparent from Figure 1.1 is that it is a linear process that treats carbon dioxide as a waste to be disposed of. This is a continuation of the unsustainable "use once and dispose of" approach that is all pervasive in twenty-first century human society. Other examples include single use plastic and non-recyclable electronic goods that contain rare chemical elements. In contrast, this book is concerned with carbon dioxide utilisation, which treats carbon dioxide not as a waste to be disposed of, but rather as a valuable resource to be recycled and reused as illustrated in Figure 1.2. According to the Lansink Hierarchy of Waste Management [9], the first approach should always be to avoid producing waste in the first place. Thus, if new materials can be produced from carbon dioxide, then we avoid new virgin fossil carbon entering the supply chain. The least preferred option is landfill, which is essentially the fate of carbon dioxide in CCS. Intermediate options include reuse and recycle and recovery of energy: the cornerstone of CDU technologies. As such, implementation of carbon dioxide utilisation represents a shift from an unsustainable linear economy to a sustainable circular economy [10]. As shown in Figure 1.2, the combustion of fuel or production of chemicals generates carbon dioxide (Table 1.1). To close the cycle and convert the carbon dioxide back into fuel requires hydrogen. At present, almost all hydrogen produced commercially is obtained by steam reforming of methane and the water gas shift reaction (Scheme 1.2), which consumes a non-renewable resource (methane) and generates carbon dioxide [11]. As such this is not a sustainable source of hydrogen. An alternative is to obtain hydrogen by the splitting of water into hydrogen and oxygen. This is not currently cost competitive with steam reforming, but is the topic of much research. For the synthesis of chemicals from carbon dioxide, other renewable reactants are required. These should be derived from biomass and an example of such a process, the synthesis of ethylene carbonate from bioethanol and carbon dioxide, is illustrated in Scheme 1.3. The synthesis of ethene from sugar cane via bioethanol is already commercialised in

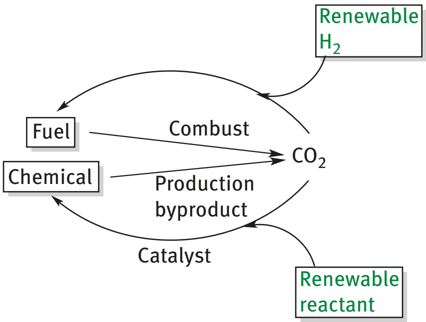
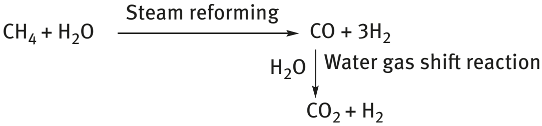
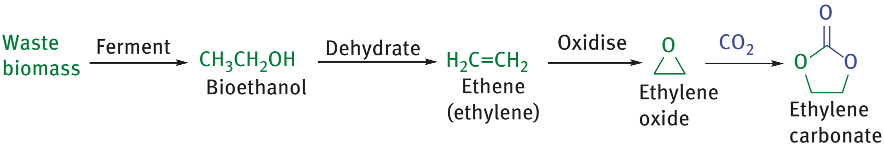


Figure 1.2: Carbon dioxide utilisation.



Scheme 1.2: Industrial synthesis of hydrogen.



Scheme 1.3: A sustainable route to ethylene carbonate.

Brazil [12], and in the USA, Croda have built a plant for the synthesis of ethylene oxide from bioethanol sourced from corn [13].

One criticism that is sometimes used to belittle carbon dioxide utilisation is the difference in scales of the energy and chemicals sectors. This difference in scale certainly exists: power generation involves the production of gigatonnes (Gt) of carbon dioxide as a by-product whilst even the largest-scale chemical processes only produce about 150 megatonnes (Mt) of product. However, as Figure 1.2 illustrates, carbon dioxide utilisation involves the conversion of carbon dioxide into both fuel and chemicals. The top circle in Figure 1.2 has the potential to be operated on the same scale as energy generation from fossil fuels and hence to make the combustion of fossil fuels obsolete. The lower circle will always be operated on a smaller scale, but here the analogy with a conventional oil refinery and with a biorefinery is informative. Figure 1.2 essentially shows a carbon dioxide refinery and Figure 1.3 compares all three types of refinery. Of these, only the oil refinery is currently operated commercially: 96% of the output of an oil refinery is fuel, the remaining 4% being chemicals that provide the basis for the current global chemicals industry. However, the 4% of the refinery output that goes to the chemicals industry generates over 40% of the profit for the oil refinery! [14] This is why it is important to consider both cycles in Figure 1.2; the route to chemicals may not consume large amounts of carbon dioxide, but it can make the whole carbon dioxide refinery commercially viable. It should also be realised that carbon dioxide mitigation can be achieved not only by capture, but also by avoidance. Under the European Union Renewable Energy Directive (RED) 2, avoidance of carbon dioxide generation is given equal status in emissions legislation to carbon dioxide captured and

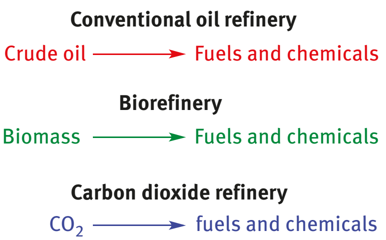


Figure 1.3: Comparison of three types of refinery.

permanently stored [15]. This is a progressive piece of legislation that recognises the precepts of the Lansink Hierarchy.

The need for a more sustainable approach to next-generation synthetic fuels and petrochemicals has been highlighted by many governments; particularly in Germany who have invested heavily in CDU, with success, through the BMBF funding instrument [16]. In May 2018, Mission Innovation published a report on Accelerating CCUS [17, 18]. This was agreed through the G20 nations and the European Union as a block. A number of “Priority Research Directions” were proposed and accepted. These include the use of carbon dioxide to make, as the EU defines them, “Synthetic Fuels of Non-Biological Origin” or “e-Fuels”. These are fuels that not only replace primarily gasoline and diesel, but which also seek to replace Jet fuel (kerosene), which is more problematic due to strict regulations on its composition. The resulting fuels, including methanol, dimethyl ether and oxymethylene ethers, have been shown to be far superior in their reduced emissions than conventional hydrocarbon fuels. The Royal Society of London have also published an excellent Policy Briefing document [19] on the Potential and Limitations of Carbon Dioxide Utilization (2017) and are due to publish a similar document on Synthetic Fuels in 2019.

There is another advantage associated with a carbon dioxide refinery: point sources of waste carbon dioxide are widely distributed around the planet and atmospheric carbon dioxide occurs at the same concentration everywhere. In contrast, large reserves of oil and gas are localised in often politically unstable parts of planet Earth and suitable land for growing biomass for a biorefinery is also not equally distributed. Thus, carbon dioxide refineries have the potential to be operated anywhere on the planet without the need to source and transport the crude oil or biomass long distances.

The importance of a carbon cycle cannot be underestimated. Nature has for millions of years prior to the industrial revolution managed its own carbon cycle. Carbon dioxide produced from combustion and natural phenomena has been used in photosynthesis to produce the energy for a plant: carbohydrate. When this is combusted or metabolised, the carbon dioxide is re-emitted and the cycle continued. However, an imbalance in the cycle was caused by the industrial revolution and the anthropogenic use of carbon-based materials as a source of fuel. It should be noted that fossil fuels originated from the decomposition of fauna and flora over many millions of years. These natural precursors came from the photosynthetic process in the case of flora and from animal metabolism in the case of fauna. Carbon dioxide in the atmosphere was the source of this carbon. We could therefore consider that what the scientists and engineers are doing in CDU is simply accelerating the fossilisation process using catalysts and process development. It has been argued that reusing carbon dioxide that has been emitted in a combustion process is still fossil carbon and therefore the product is fossil based. This neglects the fact that it is second-life carbon, re-used to produce a product that would otherwise have required virgin fossil oil. If we take the approach that products made from emitted carbon dioxide are still fossil based, then we could equally say that biomass produced in the current environment is also fossil based! Clearly there needs to be a logical disconnect between virgin fossil carbon and second and subsequent life carbon.

What is very clear is that we cannot simply look at a reaction or process in isolation. We need to consider the environmental and economic impact of the whole process across the supply chain surrounding the CDU technology. That is why this book has chapters looking at the techno-, environmental and economic impact of any process that is proposed. The public also needs to be aware of the technologies at an early stage so they are not seen as a problem. This is why this book considers the whole system, including the societal impact. While many of the technologies seem expensive at this time in comparison to fossil-based routes, one must remember that these are nascent technologies. Costs will fall as scale increases and commercial reality kicks in. Televisions and computer monitors transitioned from cathode ray tubes to liquid crystal displays. Liquid crystal display televisions cost thousands of pounds on first release (actually millions of pounds during the development phase), but can now be purchased for under 100 pounds. We should not be put off by high costs during the research and development phase.

This book has been divided into six parts. Part I introduces topics that are essential when considering carbon dioxide utilisation. These include the concept of sustainable development, social acceptance and lifecycle and technoeconomic analysis. The use of carbon dioxide as a solvent is also included in this part. Part II deals with methodologies for separating carbon dioxide from other gases, whilst Part III covers general aspects of carbon dioxide chemistry including its activation and mineralisation. Parts IV–VI contain a series of chapters each of which focusses on one way of converting carbon dioxide into a fuel or commercially important chemical. Part IV considers processes that occur with the aid of a catalyst, Part V electrochemical approaches to carbon dioxide utilisation and Part VI photochemical and plasma-induced reactions of carbon dioxide. The intention is to give the reader a flavour of what can be achieved using each of these methodologies rather than to give a comprehensive coverage. Authors were asked to concentrate the material in their chapter on processes that are already commercial, or which are closest to commercialisation. Each chapter ends with a bibliography, which the reader can use to access additional information. All chapters were written during 2018, and so the literature covered will be that published up to the end of 2017.

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