VTT Technical Research Centre of Finland

The Carbon Reuse Economy

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beyond the obvious

The Carbon Reuse Economy

Transforming CO_2 from a pollutant into a resource

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PREFACE

IN THE CARBON REUSE ECONOMY fossil carbon is left in the ground while aboveground carbon circulates without accumulating to the atmosphere. Forests act as both carbon sinks and an important source of carbon. In addition to this, carbon is captured from industrial emissions and eventually from the air, too. Our aim is that globally by 2040, three gigatons of carbon dioxide a year will be converted into fuels, chemicals, materials and food.

This document is based on the vision described above. The authors envision that carbon capture and utilisation will be one of the most important tools in helping to achieve the climate change mitigation targets determined by the Paris Agreement. However, this requires simultaneous business drivers for products manufactured from carbon dioxide. We point out some feasible pathways from carbon dioxide to products and also some barriers that still exist to the large-scale adoption of the carbon reuse economy. We believe that these barriers must be overcome, and thus propose a solution for each of them.

We also discuss the pros and cons of different product options in the carbon reuse economy. Fuels are large-volume products and thus enable large volumes of carbon dioxide to be absorbed. However, the commercialisation of low-value fuels can be more challenging compared to higher-value products. High-value materials produced from carbon dioxide may also provide an option to keep carbon dioxide out of circulation for decades. Even though in the best-case scenario carbon capture and utilisation can be carbon neutral, this longer product lifecycle might provide an additional way of slowing the carbon flux to the atmosphere during the critical period covered by the Paris Agreement targets (2020–2050). In this document we propose a timeline for the commercialisation of carbon reuse economy products based on their values and volumes.

The carbon reuse economy is inextricably linked to energy and therefore energy policies. Low carbon energy is an essential enabler for carbon reuse economy. Energy is always needed to produce value-added products from carbon dioxide, and very often these processes consume significant amounts of energy. Electrification, either direct or indirect, is needed to fulfil the targets of the Paris Agreement. It is also clear that political actions are required to promote the transformation of our energy systems.

This document has been developed in a working group comprising VTT's top experts in the field of the carbon reuse economy. In addition, internal and external workshops have been organised where many other knowledgeable experts have provided their input. The authors would like to thank all the contributors for their time and dedication.

Espoo, June 2019

Juha Lehtonen, Sami Alakurtti, Antti Arasto, Ilkka Hannula, Ali Harlin, Tiina Koljonen, Raija Lantto, Michael Lienemann, Kristin Onarheim, Juha-Pekka Pitkänen, Matti Tähtinen

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GLOSSARY

CCU
CCU is short for carbon capture and utilisation, the process by which carbon is captured from a source and either utilised on site or transported elsewhere to be used. Utilisation can be the direct use of CO_2 or its use as a raw material for the synthesis of chemical products. Often CCU does not decrease atmospheric CO_2, but delays CO_2 release. Depending on the use of synthetised product or utilisation, this delay varies from hours to tens of years. The climate impact of CCU also depends on the carbon and energy source.

CCS
CCS means carbon capture and storage, the process by which carbon is captured from a source and stored on site or often off site – for example, at a depleted gas or oil field, or other geological formation. Enhanced oil recovery (EOR) is not usually considered as CCS. Sequestrated carbon dioxide is expected to stay underground without significant release to the atmosphere. CCS does not increase atmospheric CO_2, but will not decrease it if CO_2 is not captured from the air, either directly or indirectly (bio-CCS, BECCS).

Direct electrification
Direct electrification means the electrification of processes or vehicles. Examples include electric cars or heat pumps. Direct electrification can be used as a substitute for other energy sources, for example fossil-based fuels in transportation.

Indirect electrification
Indirect electrification means the use of electricity to produce commodities that would otherwise be made from fossil raw materials, and is used when direct electrification is technically or economically unfeasible. One example is hydrogen for ammonia production, which is produced from natural gas: the ammonia production process can be indirectly electrified using water electrolysis-based hydrogen. Indirect electrification opens up possibilities for carbon-neutral products and is often also related to energy carriers and long-term chemical energy storage.

Hydrocarbon fuels
Liquid and gaseous fuels (e.g. gasoline, diesel, jet fuel) composed of hydrocarbon molecules.

Electrolytic hydrogen
Hydrogen can be produced by splitting water into hydrogen and oxygen using electrolysis. In this way the energy content of hydrogen originates from the electricity used for the electrolysis. If low-carbon electricity is used, electrolytic hydrogen can be considered carbon neutral or near carbon neutral.

Electrofuels
Electrofuels are fuels where electrical energy is stored in liquid or gaseous fuels. A typical way to produce electrofuels is to react electrolytic hydrogen with carbon dioxide. However, hydrogen itself can also be considered an electrofuel. The systemic climate impact of an electrofuel is determined by the source of electricity and carbon dioxide used to produce it.

Negative carbon dioxide emissions
Negative carbon dioxide emissions are related to technologies (negative emission technologies, NETs) where carbon dioxide is removed

from the atmosphere permanently. Negative carbon dioxide emissions are achieved when more carbon dioxide is captured than is released to the atmosphere.

ABBREVIATIONS

ADT
Air dried ton

Bio-CCS
Carbon capture and storage from processes utilising biogenic carbon sources

BECCS
Carbon capture and storage from bioenergy production

CCS
Carbon capture and storage

CCU
Carbon capture and utilisation

CCUS
Carbon capture utilisation and storage

GHG
Greenhouse gas

TRL
Technology readiness level

1

THE CARBON REUSE ECONOMY AS AN ENABLER OF A LOW-CARBON FUTURE

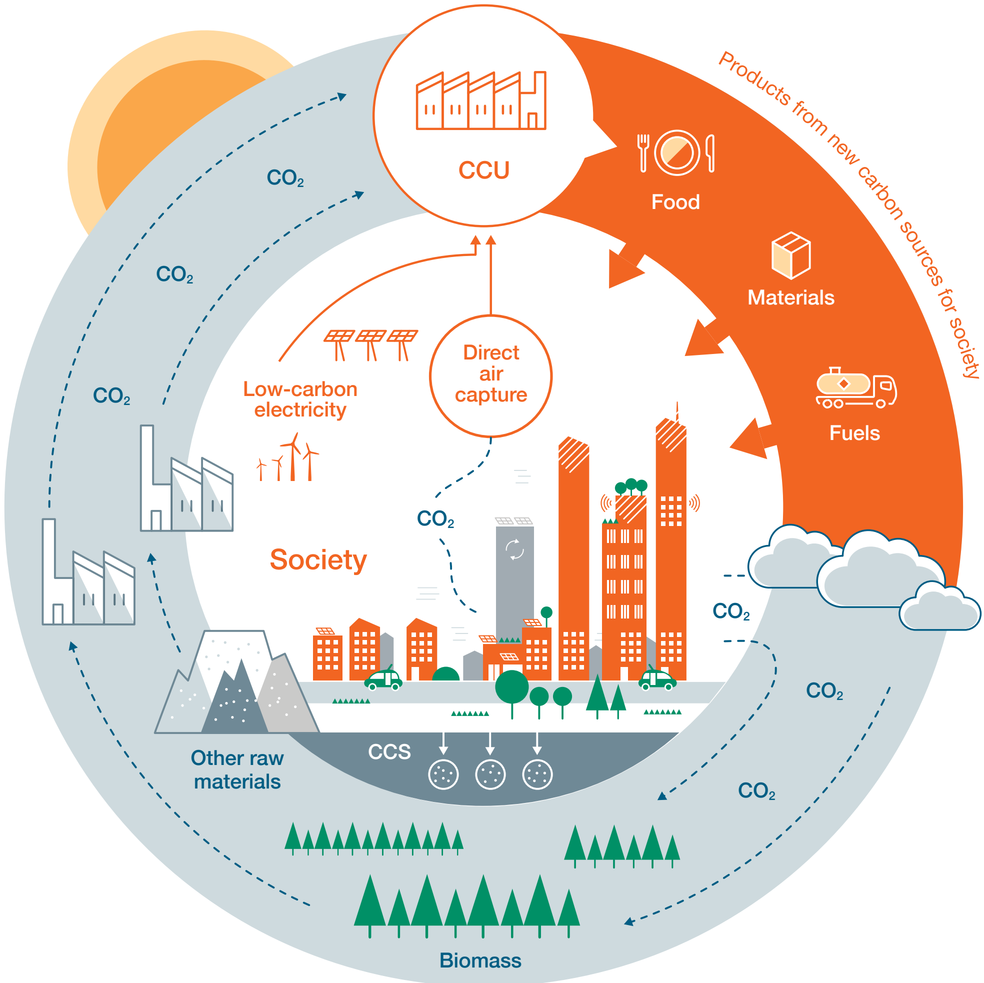

Figure 1 . Carbon cycles in a future society.

IN A FUTURE WORLD that has achieved the goals of the Paris Agreement, society is largely free of fossil carbon-based goods and services. Fossil carbon in commodities has been replaced by sustainable carbon cycles. In industrial energy supply a shift from fossil fuels to electricity and electrolytic hydrogen has taken place, while transportation relies on a combination of battery-powered electric vehicles and sustainable hydrocarbon fuels. However, a low-carbon world is not a no-carbon world as carbon will continue to be crucial for consumer commodities based on organic chemicals and materials as well as for food and animal feed. The required carbon is not taken from fossil resources but from either biomass or via the capture and reuse of the carbon content of various waste streams and products at end of life. Thus carbon capture and utilisation (CCU) is likely to begin with the utilisation of the most significant industrial point sources of CO_2 such as emissions from the cement and steel industries. After these industries have been electrified and decarbonised, capture will move towards biogenic sources. Finally, in the special case where point sources cannot provide sufficient carbon, the capture of CO_2 directly from air (direct air capture, DAC) will be realised. Carbon cycles in a future society are illustrated in Figure 1.

THE PARIS AGREEMENT

> The Paris Agreement's goal is to mitigate climate change by keeping the global temperature rise well below 2 degrees Celsius above pre-industrial levels and pursue limiting the temperature increase even further to 1.5 degrees Celsius. In addition, the agreement takes into account the impacts of climate change and the measures needed to deal with them.

Despite the shift towards electrification, many major segments in industry and transport are expected to remain reliant on carbon-based fuels and commodity chemicals for the foreseeable future. However, blast furnaces in steel manufacturing may shift from using coke to using hydrogen as the reducing agent, enabling decarbonisation of this sector. In the cement industry a shift to either biomass or electricity to power rotary kilns is expected. Furthermore, carbon capture and storage (CCS) and CCU) could offer significant opportunities to reduce carbon emissions in these sectors. While CCS has been seen as a critical component in driving down emissions from fossil fuel use, CCU can be understood as an indirect electrification strategy for situations where direct electrification is either technically impossible or prohibitively expensive. Carbon is usually captured from the exhaust gases of thermal power generators in industrial processes like cement and steel plants, or biogenic CO_2 from bioenergy production. In the most widely proposed application of CCU, electric energy is converted into chemical energy via electrolysis of water, while CO_2 is used to chemically bind the hydrogen produced into an easily storable or applicable form. There are two important parallels for such carbon reuse strategies:

- The hydrogen economy. The competition between the hydrogen (H_2) economy and the carbon reuse economy is a competition between developing a new distribution and use infrastructure for H_2 or capturing CO_2 and synthesising hydrogen-containing molecules that are compatible with existing infrastructure. They both need a renewable primary energy source, as the underlying difference is only related to the energy carrier, and infrastructure needed for that.
- Waste hierarchy. The principle of a waste hierarchy is to extract maximum benefits from products while minimising the amount of waste or preventing waste from being generated at all. Similarly, in the carbon reuse economy the principle is to reutilise carbon in a way that enables the decoupling of products and services from underground fossil carbon reserves. Figure 2 illustrates the relationship between more traditional climate mitigation options (energy conservation, energy efficiency and low-carbon technologies) and the various options available under Carbon Capture Utilisation and Storage (CCUS). Once CO_2 is captured it can either be stored underground (CCS) or reused for a range of purposes, from fuel (electrofuels) and chemical production to enhanced hydrocarbon or commodity recovery. The worst environmental outcome is also the cheapest, namely venting into the atmosphere.

In addition to indirect electrification in the transport and energy sector, most of the organic chemicals and polymers such as plastic products and synthetic textile fibres required today could be produced from carbon dioxide. Common large-scale chemical intermediates such as methanol, ethylene, propylene and BTX (benzene, toluene, xylene) aromatics, which are important building blocks for sustainable end products, can be synthesised from carbon dioxide and hydrogen. Polymers and materials with significantly longer lifetime than, for example, fuel products can play an important role as carbon-binders through CCU. However, realising this vision will require significant renewal across the petrochemical industry.

Most of the organic chemicals and polymers such as plastic products and synthetic textile fibres required today could be produced from carbon dioxide.

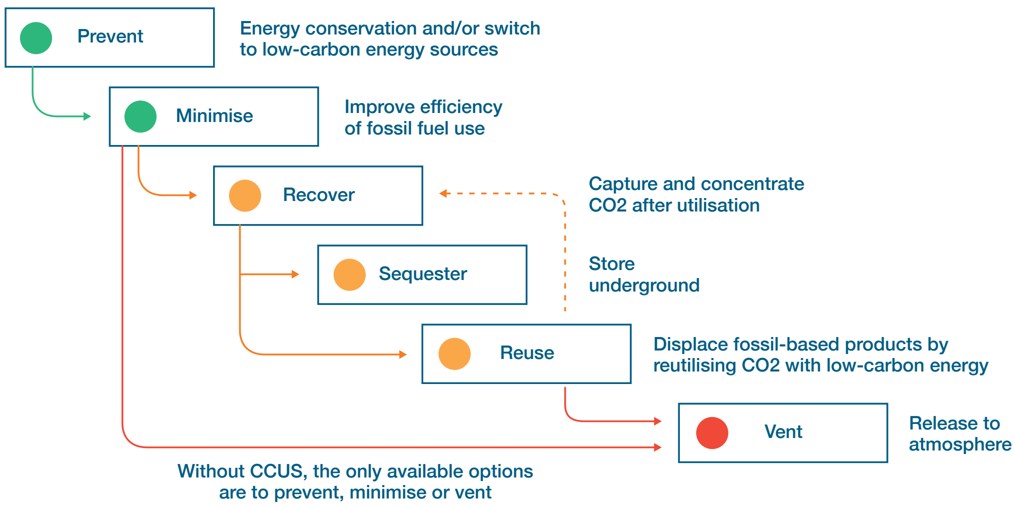

Figure 2. CCUS hierarchy according to Hannula and Reiner (2017).[2]

The drivers for bulk energy products and high-value chemicals and materials are different. The market drivers for energy and fuel products are mainly based on the need for new sustainable fuels as a result of legislative pressures such as various mandates and subsidies. For example, fuels based on CCU and low-carbon electricity (electrofuels) are included in a new EU Directive on the promotion of the use of energy from renewable sources (RED II)[3] as a new class of sustainable fuels (liquid and gaseous renewable fuels of non-biological origin). Production of chemicals and materials is mainly based on the higher market value of these products compared to fuels providing better profitability. Even though the production cost of a CCU-based product is often higher than the cost of the displaced fossil-based product, the profitability of CCU can be improved by applying green premiums to the product price, improving the properties of a CCU-based product or the reputational enhancement that green products can provide.

Since the cost and supply of low-carbon energy are the main hurdles in the commercialisation of CCU products, it is easier to commercialise products that are less energy intensive to produce.

Some CCU applications exist where hydrogen is not needed, like the production of precipitated calcium carbonate, other carbonates and heat transfer fluids. Some organic products can be manufactured from CO_2 without hydrogen when raw materials are partially of fossil origin (polycarbonate polyols, polycarbonate polyurethanes). However, due to the low share of carbon originating from CO_2 in these products the positive climate impact is limited. Despite the limitations, these products can play an important role in the commercialisation of CCU technologies. Furthermore, in some CO_2 conversion processes hydrogen demand is limited, or hydrogen can be applied to boost bio-based processes where CO_2 is released as a by-product. An example of such a process is the production of hydrogen-enhanced biofuels, where hydrogen is used to convert CO_2 formed as a by-product of biomass processing.[4] However, in most CCU conversion processes the demand for hydrogen is high, meaning that significant cheap, low-carbon electricity capacity is required to cover the needs of high-volume production of CCU-based products.

From an overall systemic sustainability aspect, achieving carbon neutrality, and especially carbon negativity, requires careful optimisation of the capture and release of CO_2. This means balancing the usage (repository) between/within the short-term, mid-term and long-term commodities and storage. This in turn means that operations can be carbon neutral or carbon negative, but if they are not managed and optimised from a systemic perspective the impact on sustainability is difficult to determine.

Still, this fact does not constrain the usage of CO_2 as a resource. For instance, in areas where agriculture is no longer viable due to loss of arable land and scarcity of water, CO_2 plays a crucial role in the production of nutritious foods. However, in the long-term utilisation of CO_2 needs to be based on low-carbon energy to help tackle climate change.

One fifth of human-caused greenhouse gas emissions originate from agriculture[5], either directly from machinery fuels and farm animals, or indirectly as a consequence of land-use change. Modern agriculture also raises many other environmental concerns: over-fertilisation has led to eutrophication of water ecosystems, and depletion of biodiversity is also a serious problem as is the sufficiency of natural resources (for example, water, soil, forests). At the same time, the need for food production is expected to grow by about 50% by

One fifth of human-caused greenhouse gas emissions originate from agriculture.[5]

2050, while climate change threatens to reduce production by 50%. The potential to further increase the land area used for cultivation is limited, as today 50% of habitable land area is already used for fields and only 37% for forests.[6] In a future society, fields and animals will not serve as the only source of human nutrition. Instead, biotechnical solutions will be used to produce food and feed with a smaller environmental footprint and with reduced land use requirements. Food production can use either direct sunlight or even electricity (through hydrogen) as a source of energy.[7] In both cases, microorganisms convert CO_2 into amino acids, carbohydrates, vitamins and lipids provided that sustainable sources of nitrogen and phosphorus are available. The bacterial cell mass produced in such hydrogen fermentations contains, in addition to compounds with nutritional value, high amounts of feedstocks for the production of biodegradable plastics (polyhydroxyalkanoates) and biofuels (lipids). The accumulation of reduced organic compounds in the biomass produced from hydrogen fermentation is indicative of a high biosynthetic potential of the microbial biocatalysts and means they can be engineered to enable the production of value-added organic compounds such as pigments, flavours and chemical feedstocks.

The three potential carbon reuse economy product pathways envisioned in this study are presented in Chapter 4. These pathways are shown in Figure 3.

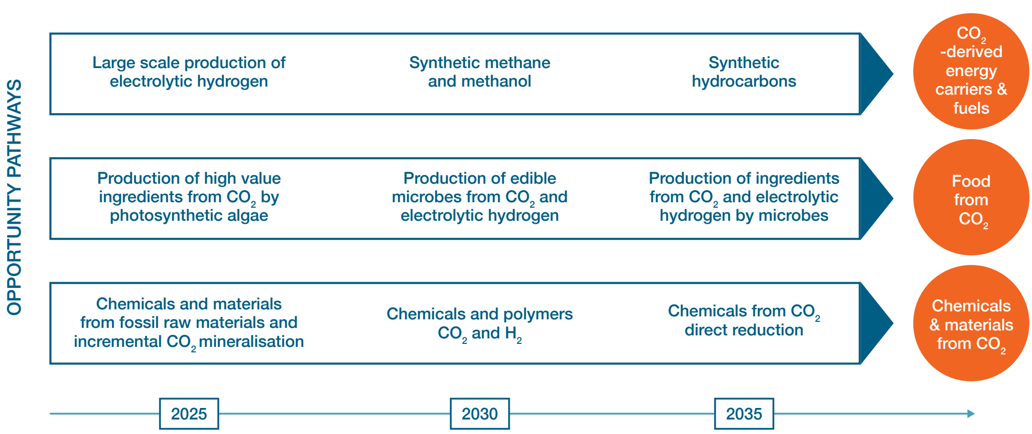

Figure 3. Carbon reuse economy pathways.

2

DRIVERS OF CHANGE

THREE MAIN DRIVERS can be identified for the carbon reuse economy: 1) the need to reduce CO_2 emissions into the atmosphere, 2) expanding regional resource bases and securing energy demand for carbon-dependent industries and 3) the potential for developing new businesses based on the sustainable supply and use of carbon.

The first driver relates to the potential of carbon reuse to displace the use of fossil resources for energy, fuels, chemicals and materials. The positive impact on the climate is realised directly through delayed CO_2 emissions (which will depend on the lifetime of the product) and indirectly via displacement of fossil raw materials. In the long term, limiting the global temperature rise to below or well below 2°C will most likely require removal of CO_2 from the atmosphere.

The second driver for carbon reuse is the potential to expand the regional raw material resource bases and secure energy supply (i.e. the energy needed to sustain societal activities). With high shares of variable low-carbon electricity, CCU could enable the introduction of additional low-carbon energy into the system and potentially add additional flexibility too. Furthermore, because most of the raw materials for fossil-based products are currently imported in many countries, CCU makes it possible to rely on domestic carbon sources.

A third important driver for CCU is the potential for new business cases based on the sustainable supply of carbon for value-added products. Economic feasibility is a long-term prerequisite for the viability and large-scale realisation of CCU concepts. In addition, there are CCU business cases, such as high-value specialty chemicals and materials that can be justified solely on an economic basis.

The above-discussed drivers are interconnected and are likely to play different roles at the local, national and global level. They can be concretised in the following eight points (Table 1).

Table 1. Drivers for CCU.

CLIMATE CHANGE	
1. Implementation of the Paris Climate Agreement	Close to 200 countries are committed to the agreement to limit global warming to well below 2° C above pre-industrial levels. New policies and regulations are needed as countries strive to meet the needed GHG mitigation targets, for example setting goals of close to zero global GHG emissions in OECD countries. In order to avoid irreversible impacts of climate change, post 2050 the net CO_2 emissions should be negative; these targets will become increasingly challenging to achieve if emission reductions are delayed.
2. Industrial renewal	Fuel use and chemical reactions in industry are a major source of carbon emissions. In the coming years, the pressure to reduce industrial carbon emissions will increase and the electricity sector will be decarbonised. CCS is a key technology for reducing industrial emissions, but the implementation of CCS has faced repeated setbacks in the past decade. In the absence of political support for underground storage of CO_2, CCU could offer an alternative route for emission reductions and an alternative, sustainable carbon source for industries based on the production of carbon-based commodities.
3. Low-carbon mobility	In addition to industry, the decarbonisation of transport presents a particular challenge for climate change mitigation. Electric vehicles are emerging as a competitive option for short distances, but their competitiveness quickly deteriorates at higher ranges where sustainable liquid and gaseous fuels offer a lower-cost option.[2] Air, marine and heavy road transport in particular are challenging to electrify directly. Electrofuels like methane, methanol and liquid hydrocarbons, together with biofuels, will have an important role in solving these challenges.
SUSTAINABLE RESOURCE BASE EXPANSION	
4. Implementation of a circular economy	A resource-sufficient and low-carbon society is needed in a world where the use of fossil raw materials has largely been phased out. In addition to the use of biomass, the carbon reuse economy offers a new carbon source for the production of chemicals, fuels and materials as well as food and animal feed.

5. Loss of biodiversity	Today, biomass is used as a non-fossil carbon source in the production of energy, fuels and materials. However, climate change-accelerated loss of biodiversity, an increasing need for food and animal feed as well as other sustainability concerns will increasingly limit its use (both field and forest biomass). Captured carbon dioxide can be used as an alternative source of sustainable carbon in these applications.
BUSINESS DRIVERS	
6. Need for seasonal energy storage	Large-scale penetration of variable renewable energy (VRE) in the energy system may require technologies and systems for large-scale energy storage that can mitigate long-term energy imbalances. On the other hand, the renewal of electricity markets to ensure market-based investments in renewable energy solutions, back-up capacity and storage is a prerequisite for achieving a high share of VRE.
7. New policies and markets for new commodities driven by social change and increased awareness on sustainable development	Transitioning to the carbon reuse economy requires sustainable carbon and energy sources. This kind of radical change is not possible without social change and awareness of sustainability in everyday life and business. Social acceptance will also drive the implementation of new policies to phase out fossil fuels.
8. Rapidly declining cost of variable renewable energy (VRE)	The global energy system is currently in transition, driven by reductions in the generation costs of VRE sources such as wind and solar, and political efforts to shift to a low-carbon society by cutting GHG emissions to the level agreed in the Paris Agreement. Today the cost of VRE has already reached, or is approaching, the cost of conventional power and heat generation options in many locations around the globe. As this trend is likely to continue, it will eventually lead to high shares of VRE in the energy system and promote significant direct and indirect electrification across all sectors of the economy where technically possible.

3

PRODUCT OPTIONS IN THE CARBON REUSE ECONOMY

CO_2 CONVERSION TECHNOLOGIES can be divided into biotechnical and chemical/catalytic conversion approaches. Biotechnical routes for CO_2 conversion offer potential for higher value, lower-volume products and food ingredients, whereas chemical routes are suitable and more efficient for bulk products such as fuels and base chemicals. This is because the solutions applied in bioprocesses are typically diluted, meaning that large reactor volumes are required for production. On the other hand, biotechnical routes are typically quite selective for desired products whereas multiple reaction steps are often needed in chemical processes, which lowers the selectivity. In general, both biotechnical and chemical technologies should be considered as potential CO_2 conversion processes, but the feasibility of these technologies varies case by case. The Technology Readiness Level (TRL) of many CCU technologies is close to commercial production; however, so far only a few CCU technologies have been commercialised due to a lack of realistic business cases.

3.1 CHEMICALS AND MATERIALS

There is a vision of a future in which CO_2 becomes an increasingly important feedstock for manufacturing commodity chemicals. By utilising CO_2 for chemicals and materials, it is possible to keep carbon within a cycle for longer compared to fuels. One potential motivation for chemical companies to invest in the carbon reuse economy is the opportunity to continue to supply commodity chemicals that have traditionally relied on petrochemical feedstocks. By fast-tracking development in the area of CO_2 utilisation for commodity chemical production, chemical companies can reconsider their value chain and processes at the same time as reducing CO_2 emissions.[9,10,11] However, there needs to be a clearer long-term strategy and a stable research and industrial policy framework with the help of public funding[12] to achieve this goal.

3.1.1 CHEMICAL AND CATALYTIC CONVERSION

Some carbon dioxide-based chemicals are already produced by chemicals routes, with the largest volume product being urea. However, the ammonia used in urea production typically originates from hydrogen produced by fossil methane steam reforming, a process that releases a significant amount of carbon dioxide. Therefore, the positive climate impact of this process is still limited, though its carbon balance can be improved by capturing carbon dioxide from hydrogen production or by using hydrogen produced with low-carbon electricity.

Other organic products currently manufactured from carbon dioxide include certain carbonates (e.g. dimethyl carbonate, ethylene carbonate and propylene carbonate) and salicylic acid. Several companies are investing in technologies for the production of polycarbonates, polycarbonate polyols and polyurethanes.[13,14,15] For example, Covestro has announced commercial production of these products for mattresses.[16] Some of the raw materials in these concepts (such as epoxides and isocyanates) do however originate from fossil-based resources.

In mineralisation, carbon dioxide is reacted with metal cations (calcium or magnesium) to obtain inorganic carbonates. This mineral carbonation can be used as carbon storage instead of CCS, which has various safety and sustainability concerns. Alternatively, these inorganic carbonates can be used for construction materials or fertilisers.

The most significant routes to organic chemicals by chemical and catalytic conversion are presented in Figure 4.

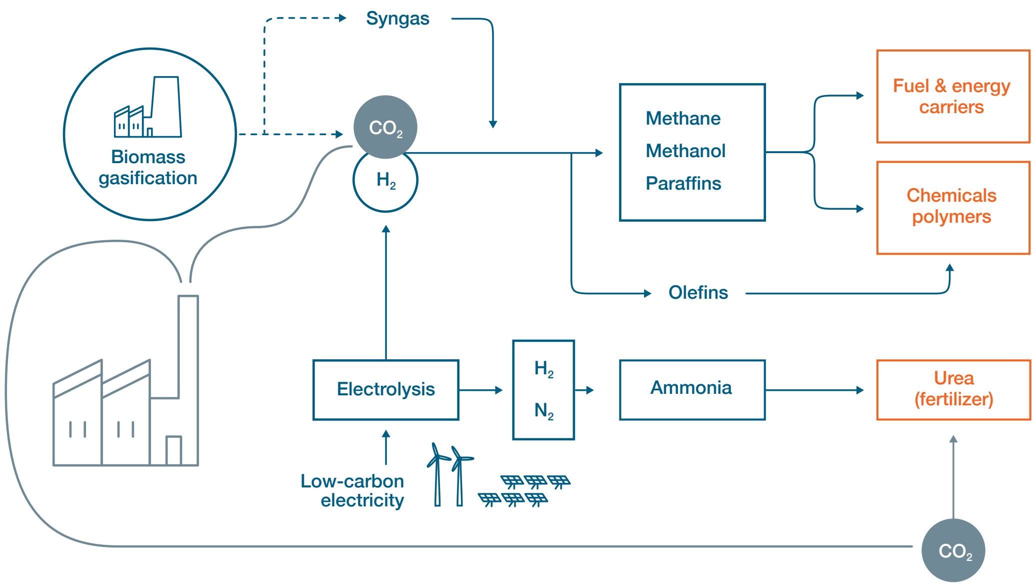

Figure 4. Routes from carbon dioxide to organic chemicals.

3.1.2 BIOLOGICAL CONVERSION

There are at least a billion different bacterial species in the world and most likely a similar number of other microorganisms. This biodiversity enables organisms that can use an enormous range of resources as their energy and carbon sources – other one-carbon compounds can be used as carbon sources in addition to carbon dioxide. The gas streams can be valorised with process concepts like gas fermentation. In gas fermentation, microorganisms work as catalysts to produce fuels such as ethanol, chemicals such as lactic acid and single-cell proteins or simple microbial cell masses for food or animal feed. The different biological routes for one-carbon compound utilisation are illustrated in Figure 5.

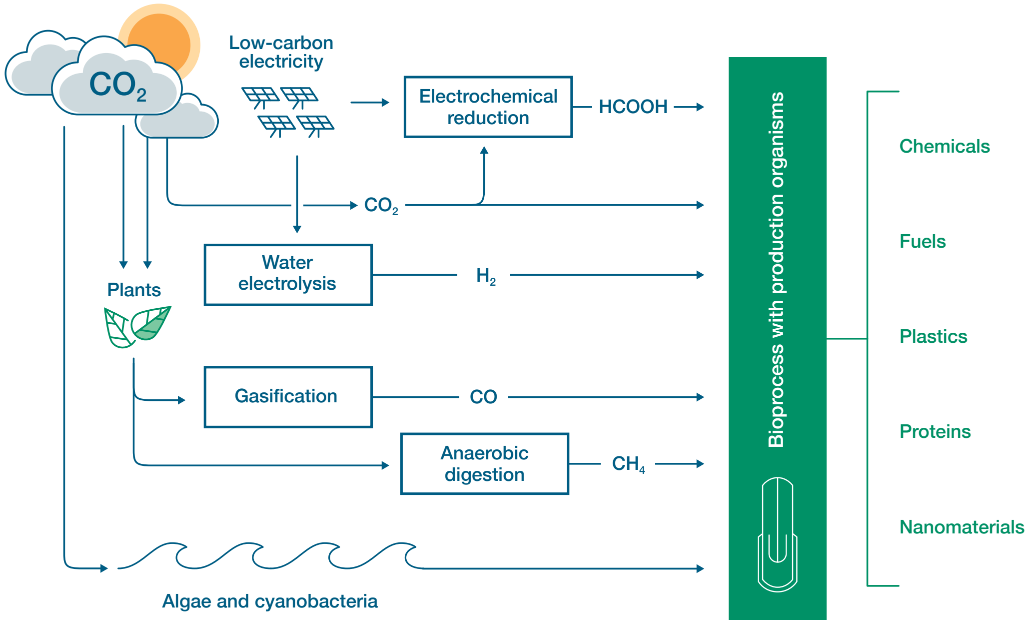

Figure 5. Different biological routes for carbon dioxide and other one-carbon compounds.

3.2 ELECTROFUELS

Fuels can be directly produced from carbon dioxide and hydrogen by catalytic processes. The most interesting concept involves the production of hydrogen from water with low-carbon electricity.[19,20,21] Various sources for CO_2 can be conceived, such as direct capture from the atmosphere, often referred to as direct air capture (DAC), or capture from the exhaust gases of thermal power generators, industrial processes like cement, steel and pulp plants or biogenetic CO_2 sources (for example biogas production). It is important to emphasise that production of fuels from atmospheric carbon dioxide does not entail permanent removal of carbon from air, but rather is an active recycling of carbon dioxide between fuel and the atmosphere. Figure 6 shows the carbon cycle of CCU fuels' manufacture together with the energy inputs and outputs required to drive it. Because carbon itself circulates in the process, the environmental impacts

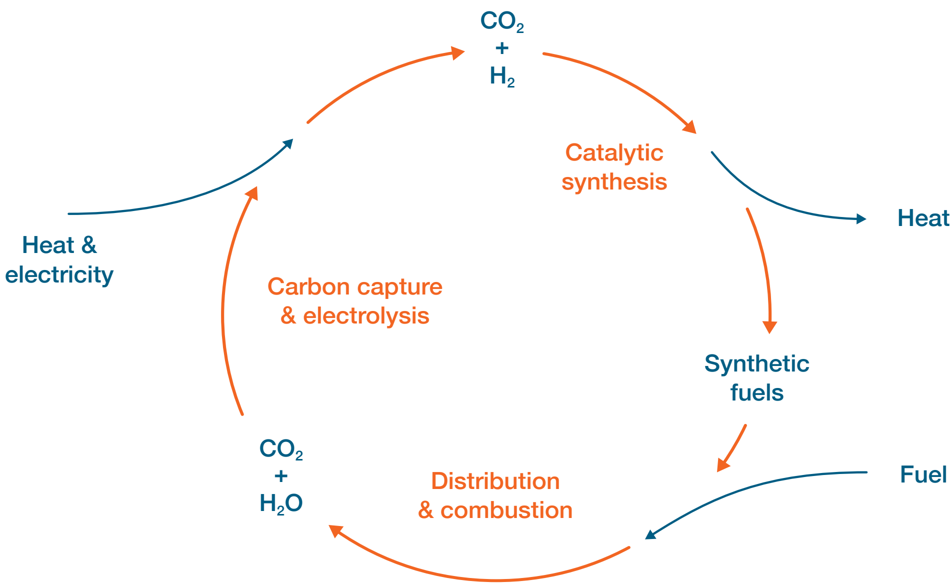

Figure 6. Carbon cycle for the manufacture of synfuels from carbon dioxide and water with electricity.

are governed by the GHG emissions associated with the provision of net energy inputs to the cycle. If the sum of these emissions is lower than the emissions of the fuels being displaced, then carbon savings have been attained.

A wide variety of fuels and energy carriers can be produced synthetically from carbon dioxide. The most common options are methane, methanol and Fischer-Tropsch (FT) hydrocarbons. Methanol can be further converted to gasoline-range hydrocarbons, for example, whereas FT hydrocarbons can be refined to high-quality traffic fuels (gasoline, diesel, jet fuel). There are already some existing and planned demonstration activities for fuel and energy carrier production from CO_2. Two CCU demonstration projects are of particular interest due to their configuration and size: the Audi e-gas (methane) plant in Germany and CRI's George Olah plant (methanol) in Iceland.

A wide variety of fuels and energy carriers can be produced synthetically from carbon dioxide.

4

PATHWAYS TO THE CARBON REUSE ECONOMY

MANUFACTURING OF BOTH bulk and specialty products from carbon dioxide can be justified from both an environmental and a business point of view. It can be expected that commercial utilisation of carbon dioxide as raw material will begin with small-scale production (large pilots or small commercial plants) of high-value products such as fine and specialty chemicals. Higher value and smaller scales are needed for profitability and especially to justify the investment. Later, the production will be extended to bulk chemicals and polymers and finally to energy and fuel products (Figure 7).

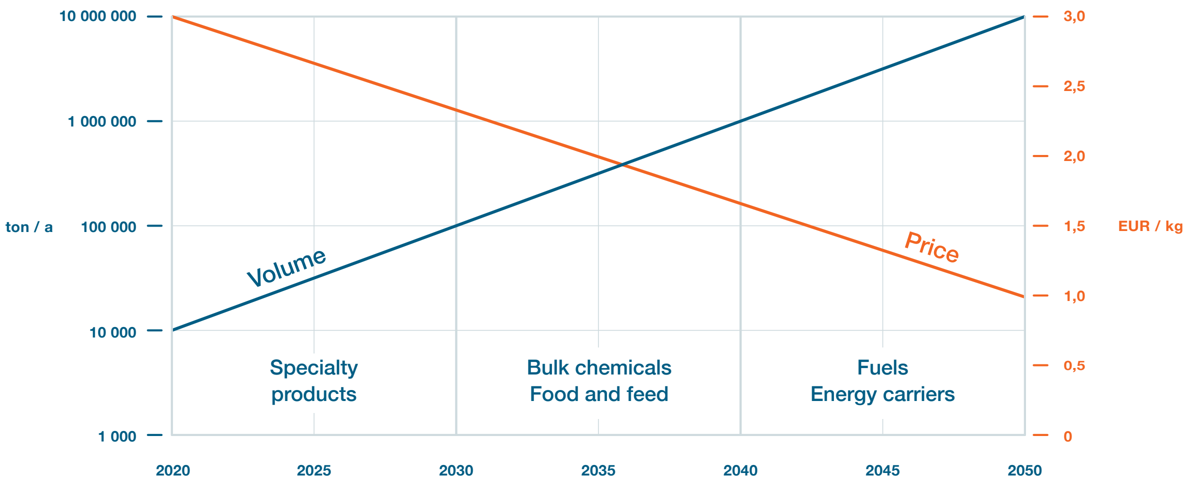

Figure 7. Evolution of the carbon reuse economy.

In the following section we present the three pathways for the realisation of the carbon reuse economy introduced in Figure 3 (chemicals and materials, food, energy carriers and fuels). We see that the realisation of all three pathways is probable and needed from the point of view of climate change mitigation. However, the commercialisation timeframe presented in Figure 7 will be different for these pathways, mainly due to economic drivers and barriers.

4.1
PATHWAY 1. CHEMICALS AND MATERIALS FROM CO_2

Carbon is the most important building block for value-added products such as chemicals and materials. Almost all chemical products currently manufactured from fossil raw materials can be produced from carbon dioxide. Furthermore, production of high-value products like carbonate polymers or platform chemicals may improve the overall economics of CCU. On the other hand, high-value products with limited hydrogen need, for example inorganic products from mineralisation, may be commercialised first. Finally, progressing decarbonisation will lead to added-value CO_2-based chemicals and materials that in turn enable the carbon reuse economy.

Almost all chemical products currently manufactured from fossil raw materials can be produced from carbon dioxide.

The forest industry is a significant emitter of biogenic carbon dioxide in the Nordic countries. Annual emissions from individual pulp mills can easily total several million tons. Therefore, these sites can be considered as potential point sources of CO_2 for the production of specialty products to be utilised on site in particular. In this way the economics of forest biorefineries can be improved. This will require a rethinking the concept of the Kraft pulp mill to incorporate better utilisation of carbon dioxide. In the following case, a pulp mill is used as an example environment for the commercialisation of chemicals and materials produced using CCU.

CASE

Chemicals and materials by pulp mill integrated Bio-CCU

More than two-thirds of the pulp produced in Europe is produced through chemical pulping processes, predominantly the Kraft pulping process.[24] By-products of the Kraft pulping process include bark and lignin, which are both combusted on site to provide the necessary heat and electricity for the pulping processes. As such, the Kraft process is largely self-sufficient in terms of energy, and may even be able to export excess electricity and heat to surrounding industry and cities. Less than half of the carbon in the raw material ends up in the pulp yield, but more effective processes for fractionating lignocellulose are expected to improve the material yield in the future. Improved processes could enable the production of novel value-added products from the pulp and paper industry. Figure 8 illustrates a typical carbon flow in CO_2 equivalents for a modern Kraft pulp mill producing 800,000 ADT market pulp annually.

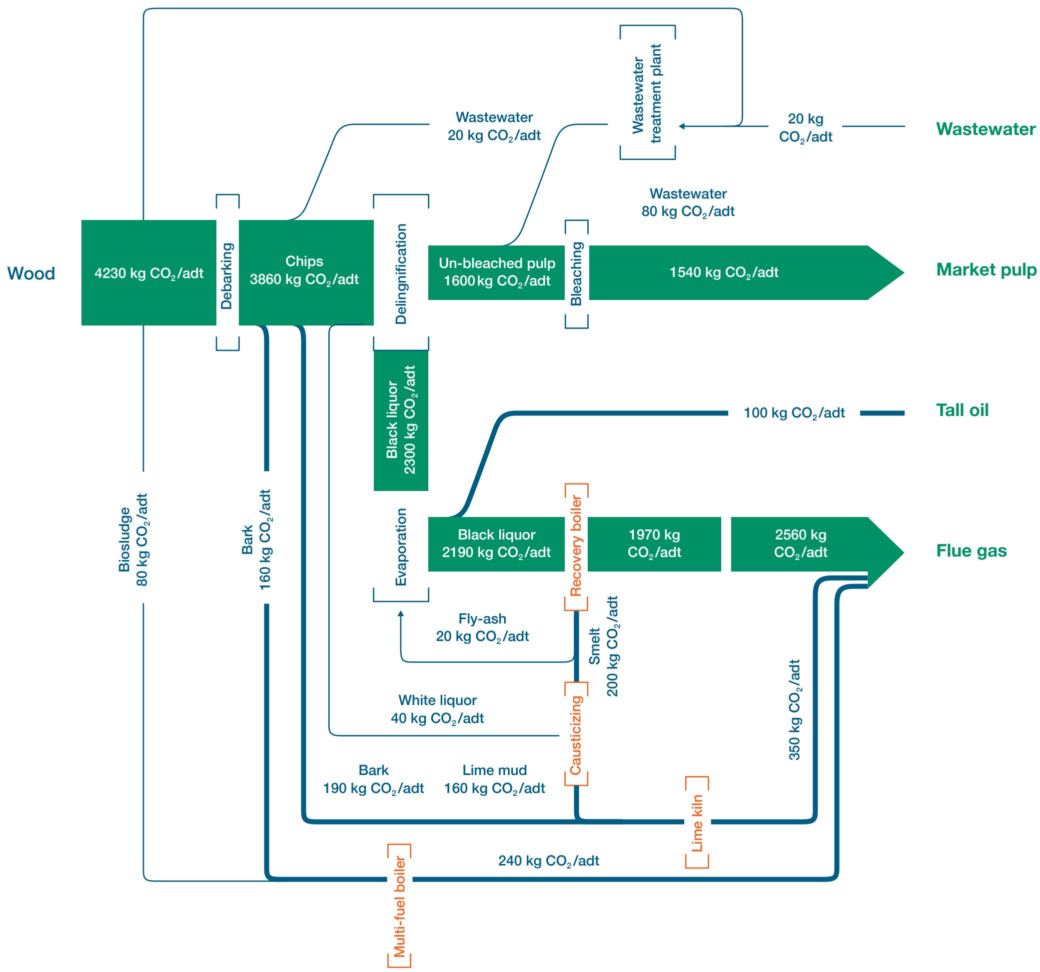

Figure 8. Carbon flow of a Kraft pulp mill producing 800,000 ADT/year market pulp.

The majority of the remaining carbon goes through various combustion processes and ends up as CO_2. A Kraft process typically emits 2.5–3.0 tons of CO_2 per air-dried ton (ADT) of pulp. There are three main sources of CO_2 emissions at a Kraft pulp mill: the recovery boiler combusting black liquor based on lignin, the multi-fuel boiler combusting bark from debarking raw material and the lime kiln, which can be operated by either fossil fuel (heavy fuel oil) or biomass, for instance syngas from bark gasification. Depending on the fuel input to the lime kiln, most modern Kraft pulp mills are fossil free, and thus 75–100% of the CO_2 emissions from the Kraft process are of biogenic origin, which enables recycling of biogenic carbon.

The potential for CCU in the pulp and paper industry mainly relates to the use of CO2 from flue gases. Using CO2 from the processes as feedstock in other processes maximises the material yield of the mill by concentrating more carbon from the raw material to the product portfolio and thus reduces direct emissions from the mill. The economic feasibility of the concepts largely relates to the need for electricity for hydrogen production and the selling price of the CCU product. A typical value chain for the CCU process in a pulp mill is illustrated in Figure 9.

The following chapters introduce the production of three important base and speciality chemicals from carbon dioxide (formic acid, methanol and polycarbonate polyols) to be integrated into a pulp mill. Furthermore, the feasibility of production is evaluated based on the price of the electricity required for production.

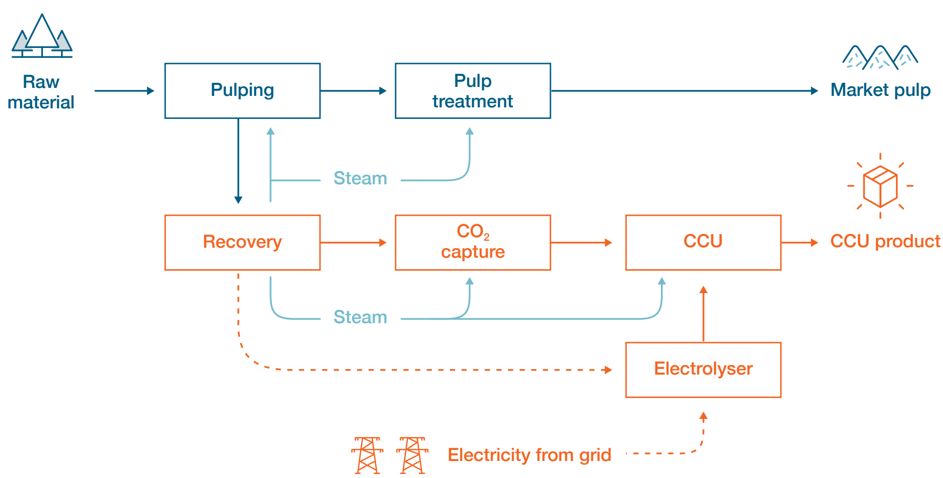

Figure 9. Value chain for CCU processes at a pulp mill.

Production of a preservative chemical from pulp mill CO_2

Formic acid is a carboxylic acid (HCOOH) and can be applied as such, for instance as a preservative in the production of leather, dyes or rubber, or it can be used as a chemical intermediate. The global market of formic acid market is relatively small, with less than 1 Mt/a production volume. Consequently, only a small stream of CO_2 is needed to satisfy a regional market. A typical formic acid plant produces 100,000– 200,000 t/a. Formic acid is commonly produced via methyl formate by carbonylation of methanol from fossil raw materials, followed by a series of further reaction steps. Formic acid can be produced from CO_2 by applying amines and homogeneous catalysts according to the following equation:

$$CO_2 + H_2 + C_{18}H_{39}N \leftrightarrow C_{18}H_{39}N - HCOOH \leftrightarrow C_{18}H_{39}N + HCOOH$$

Formic acid production from CO_2 is currently at TRL level 3–4. The formic acid production process requires additional steam from the pulp mill and electricity for hydrogen production, if the hydrogen is produced via electrolysis. Production of formic acid from CO_2 captured via post-combustion processes from flue gases could be economically feasible due to several factors. The small amount of CO_2 to be converted into formic acid translates into a low need for hydrogen and thus for additional electricity. In addition, formic acid has a relatively high selling price, around €650/t. For a Kraft pulp mill producing 800,000 ADT/year pulp at a levelised price of around €522/ADT, the revenue derived from a formic acid production level of 133 kton/year would result in a decrease in pulp cost of around 10%. A formic acid plant of this size would be small enough to be powered with excess electricity from the mill.

Production of a versatile chemical intermediate and fuel integrated into a pulp mill

Methanol (CH_3OH) is an alcohol that can be used directly as a fuel or as an intermediate for other chemicals such as formaldehyde, acetic acid and fuel ethers (MTBE, TAME) used as octane boosters in gasoline. The market for methanol is large and growing. Methanol is typically produced from synthesis gas from natural gas or is produced from carbon dioxide by hydrogenation reactions applying supported metal catalysts according to the following reaction equation:

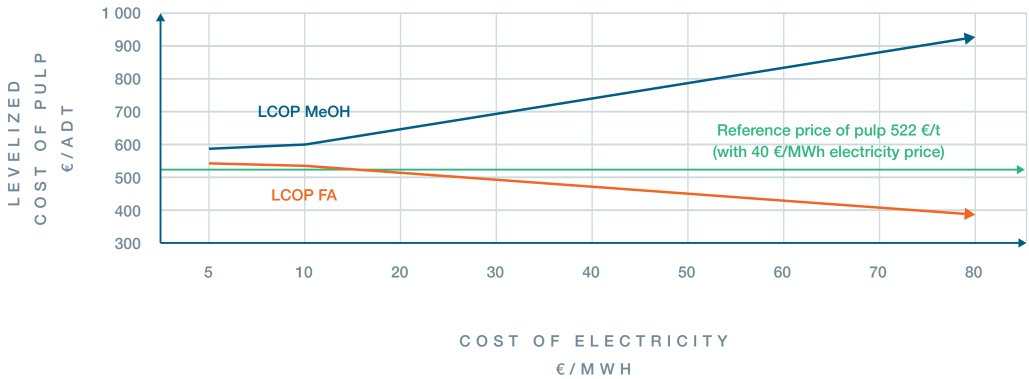

Figure 10. Sensitivity of levelised cost of pulp to electricity cost with formic acid, methanol and polycarbonate polyol production.

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

The conversion of CO_2 into methanol is hydrogen intensive and the process requires significant amounts of electricity. In addition, the selling price of methanol is relatively low, around €350/t. Combining these two factors, investing in CO_2 capture and methanol synthesis processes at a Kraft pulp mill is probably not feasible. Calculated under the same assumptions as formic acid, the methanol production for a methanol plant size of around 500 kt./year would result in an increase in the levelised cost of pulp of more than 40%. The sensitivity of CCU processes at a Kraft pulp mill to the cost of electricity is illustrated in Figure 10.

Manufacturing chemicals and materials with high CO2 content for running shoes and other commodities

Polyurethanes are versatile materials with many different applications. They are produced from two raw materials: isocyanates and polyols. Polycarbonate polyols (PC) are typically used for polyurethanes suitable for most challenging applications such as coatings, elastomers, adhesives and foams.[26] Polycarbonate polyols have been traditionally produced from phosgene and monomeric diols. However, due to the high toxicity of phosgene, alternative, more environmentally friendly polycarbonate polyol production processes are needed. Polycarbonates and polycarbonate polyols can also be produced from carbon dioxide and epoxides.[27] This new route can be based on captured CO_2, and it has been recently introduced by several companies[13,28] aiming for different polyurethane-based products. Covestro has introduced industrial production of polyether polycarbonate polyols, which are used for polyurethane foams.[16] The main applications for these foams are mattresses and furniture. However, because two out of the three raw materials used to produce these polyurethanes are fossil based (epoxides, isocyanates), the carbon dioxide content can only be increased by 20%.

Instead of using fossil-based epoxides, they can be produced from CO_2-based olefins. Light olefins suitable for epoxides can be manufactured catalytically from CO_2 and hydrogen applying VTT Fischer-Tropsch technology. As a result, polycarbonate polyols with >90% and polyurethanes with >50% carbon content originating from carbon dioxide can be obtained. This will open up a market for various materials with high carbon dioxide content to be applied in various consumer products, such as running shoes. The value chain from carbon dioxide to polyurethane foams is presented in Figure 11.

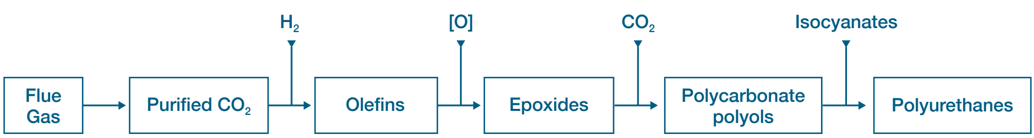

Figure 11. Value chain for polycarbonate polyols and polyurethanes.

4.2 PATHWAY 2: FOOD FROM CO_2

Food shortages will become a serious problem due to concomitant population growth and declining traditional food production caused by the effects of climate change. Livestock will be at risk because diminishing food and edible feed reserves will be primarily used for people. Technological measures have already been taken to limit CO_2 emissions and to use captured CO_2 to boost food production. The alternatives to carbon capture and utilisation are a) natural photosynthesis by plants and algae at first and b) other synthesis routes, for example microbial electrosynthesis, later (Figure 12). Apart from CO_2, photosynthesis also requires sunlight and water. A microbial conversion of CO_2 into food components, such as protein, sugars and other carbohydrates and lipids, basically mimics nature's own way of producing multiform biomass. Currently the most interesting synthesis routes include the exploitation of microbes using CO_2 and sunlight and microbes using CO_2 and hydrogen. The ability of certain autotrophic microbes, with the help of electricity, to reduce CO_2 to simple hydrocarbons, such as methane or methanol, has been known for many decades.[29,30]

A microbial conversion of CO^2 into food components, such as protein, sugars and other carbohydrates and lipids, basically mimics nature's own way of producing multiform biomass.

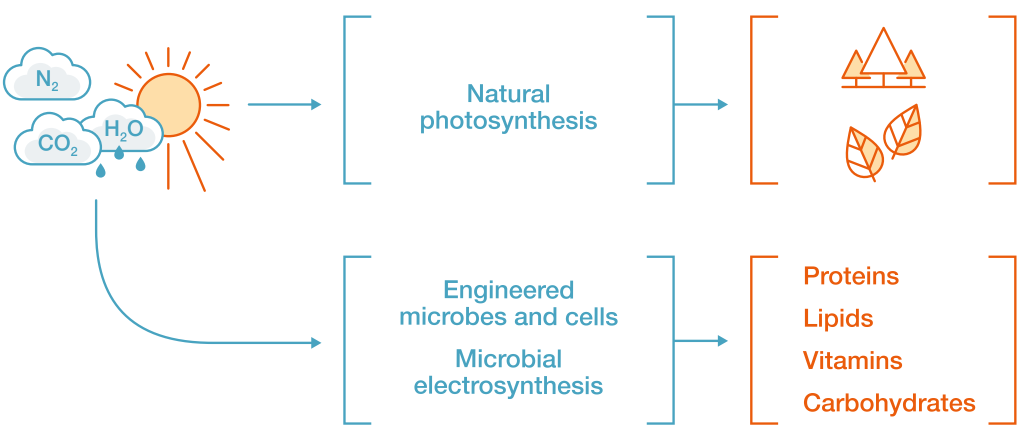

Figure 12. Alternative routes from carbon dioxide to food.

Firstly, CO_2 is captured from flue gases and used as a carbon source for edible photosynthetic plants and algae cultivated in controlled and closed environments. It is predicted that production of edible plants will move from arable land to greenhouses and algae to bioreactors at accelerating speed. Use of captured CO_2 for crop or algae cultivation is self-evidently a more sustainable alternative than just sequestering CO_2 underground. Integrating greenhouses and algae bioreactors into waste incineration plants or biogas plants, for example, can efficiently balance the CO_2 emissions down to zero. This technological concept has already been developed to a commercial scale.[31]

When technological solutions are mature enough, business life and individuals are more open minded and there is a real shortage of nutritious food, we can start using captured or atmospheric CO_2 as a raw material for the second-phase food production, i.e. converting CO_2 to microbial biomass for food use by electrosynthesis. Food production is decoupled from agriculture, livestock husbandry and aquaculture. In turn this will partially solve the challenges related to land use, eutrophication of water systems, overfishing and climate change. The environmental impacts are minimised to zero, and eventually solutions for producing personalised and nutritious food at home will be realised, although centralised closed, controlled and optimised food production “farms” will also emerge. Food production will no longer be dependent on any specific temperature, humidity, soil type or region and, as such, food sources can also be provided in locations that suffer from famine and lack of arable land due to drought and erosion.

4.3 PATHWAY 3: CO_2-DERIVED ENERGY CARRIERS AND FUELS

Carbon is the most important building block for liquid and gaseous fuels and large volumes of carbon can be bound to large-volume energy carriers and fuels. However, a significant amount of energy is needed to convert carbon dioxide into higher value products. The energy content of CO_2 can be increased through its reactions with energy-rich molecules such as hydrogen. Sustainable CO_2-based products can be produced using low-carbon energy such as solar or wind energy, but cheap low-carbon energy availability is the main hurdle in the commercialisation of CCU technologies.

4.3.1 A FUTURE SOCIETY WHERE FUELS ARE PRODUCED FROM CO_2 AND LOW-CARBON HYDROGEN

A society that relies on fossil resources does not have any incentives to use CO_2 as a raw material due to either the low price of fossil resources or the economic infeasibility of using CO_2 as a raw material. Certain changes are needed in global energy flows for CO_2 to become a viable raw material for fuels. Use of fossil resources could be decreased and abandoned altogether if the price of these resources is high, laws and regulations restrict it or the availability of resources are depleted. The transition to a carbon reuse economy is dependent on the low-carbon economy transition and it requires a rapid increase in emission-free energy that allows sustainable utilisation of CO_2, for example for fuels.

In future, the release of CO_2 from fuels should be in balance with production, meaning that the amounts released to the atmosphere, captured and stored should be calculated to ensure the sustainability of CCU.

A value network and business model could rely on monitoring the energy content of the product from raw materials to product and recapture. Therefore, processed material stock could be the place where the balance of the fuel production is calculated and controlled. For instance, users of the fuel pay per energy potential of the fuel to the producer and the producer is responsible for recapture and reproduction.

This kind of business model promotes sustainable fuel production in a society where emission-free energy and CO_2 capture would be inexpensive and easily accessible. The price of fuels may increase in a way that concentrates their usage on places of the highest value generation. The possibility of insufficiency in fuel availability will direct companies to start self-production if secure availability of large amounts of fuel is critical to their core business. Good examples could be aviation or energy intensive industries in remote locations.

The value network for using CO_2 as fuel can be initiated before radical changes start in energy-related industries. These value networks may rely on subsidies or other value generation methods, such as public relations as well as brand or sustainability communications. Following two cases present solutions for the realisation of the vision.

CASE

Modular decentralised production of hydrocarbon fuels from carbon dioxide and hydrogen

Fischer-Tropsch synthesis (FT) is a technology for producing hydrocarbons from synthesis gas (carbon monoxide, hydrogen). It can also be applied to captured carbon dioxide and electrolytic hydrogen as feedstocks. However, FT has traditionally required plants with large production volumes in order to be profitable. A new concept based on a modular production unit using micro-reactor technology and efficient solid catalysts enables profitable production of hydrocarbons suitable for transportation fuels on a smaller scale. Such a unit can be located next to industrial CO_2 emission sources and production sites where surplus hydrogen may be available. This concept is presented in Figure 13. Hydrocarbons produced in these decentralised units can be upgraded to drop-in transportation fuels (electrofuels) in oil refineries. This con-

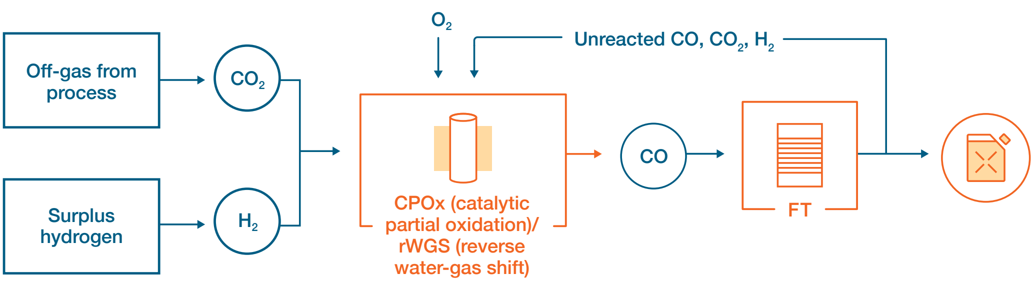

Figure 13. Modular concept for producing hydrocarbons from carbon dioxide and hydrogen.

Figure 14. Containerised pilot unit for the production of hydrocarbons from carbon dioxide and hydrogen.

cept has already been demonstrated with a mobile modular pilot plant located inside a sea container (Figure 14). The container can be transported for demonstrations using the CO_2 streams available at the sites.

CASE

Boosting of the biomass to liquids (BTL) process by low-carbon hydrogen

One interesting approach would be to integrate the manufacture of electrofuels and biofuels into a single process where CO_2, as a by-product from biomass processing, is converted to additional fuel with electrolytic hydrogen (Figure 15).[4] This means that a higher proportion of the carbon contained in the biomass can be converted to fuels, rather than vented to the atmosphere as CO_2. Such *hydrogen enhancement* would lead to an up to 2.6 or 3.1-fold increase in the biofuel yield depending on the plant configuration. This would also significantly increase the efficiency with which the biomass can be used, thereby contributing to a reduction in the biomass feedstock needed to supply the end uses.

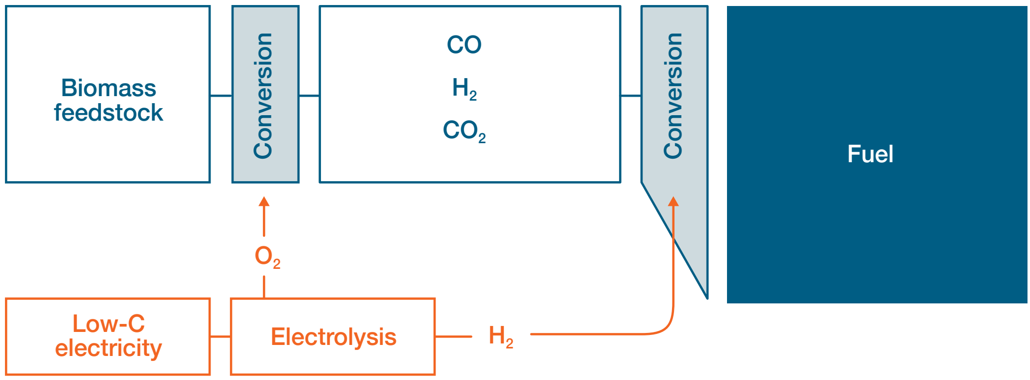

Figure 15. Concept for using electrolytic hydrogen to increase biofuel production at a gasification plant.

In the case of biomass gasification, some process integration benefits can also be foreseen, for example the elimination of a dedicated water-gas shift conversion step and an air separation unit as oxygen demand could be satisfied with by-product oxygen from the electrolyser. A less intensive form of integration could also be realised by using an external hydrogen supply only to adjust the stoichiometry of the synthesis gas.[32]

Hydrogen-enhanced biofuel processes have been found to become economically attractive over non-enhanced designs when the cost of hydrogen falls below 2.2-2.8 €/kg, again depending on the process configuration.[4] Koponen and Hannula[33] investigated the GHG emission balances of hydrogen-enhanced biofuels using the calculation method provided in the European Union's sustainability criteria for biofuels. The required 70% emission saving compared to fossil fuels was achieved when the carbon intensity of electricity remains under 84–110 gCO_2/kWh. So as with non-biomass based electrofuels, the viability of hydrogen-enhanced biofuels depends on the access to a low-cost ultra-low-carbon electric power system, or to low-carbon electric generators with high annual availability.[2]

5

RECOMMENDATIONS AND SOLUTIONS TO OVERCOME BARRIERS IN THE CARBON REUSE ECONOMY

SEVERAL BARRIERS to the wider deployment of the carbon reuse economy can be identified. They relate to the drivers described above and boil down to the ability of building up economically viable cases in the existing or future operational environment. The challenge for wider deployment comes from timed implementation, together and in synchronisation with the systemic transformation, and the ability of society to internalise most external costs related to the above listed driver groups, for example climate and a sustainable supply of raw materials. These barriers are described below together with recommendations and solutions to overcome them.

1. The cost of low-carbon energy

The cost of CCU products are predominantly determined by the price of low-carbon electricity. Previous assessments have shown that CCU concepts become feasible after low-carbon electricity becomes continuously available at a cost below 20–30 €/MWh.[4,32] **Solution: The price of low-carbon electricity is expected to decrease due to increasing investments and governmental actions and meet the target level by 2030.**

2. Primary energy supply

In contrast to direct electrification, which often reduces primary energy demand, indirect electrification will usually increase primary energy demand (Figure 16). This is likely to cause supply problems if CCU technologies are to be widely deployed, given the challenges related to decarbonisation of conventional electricity use. **Solution: Investment in low-carbon electricity should be promoted by the policies of governments.**

3. Failures in pricing fossil carbon leads to immature markets for carbon reuse compounds and materials

There are ample resources of fossil fuels that will keep the price down for decades to come. Putting a price on fossil carbon is needed to incentivise sustainable alternatives. **Solution: The pricing of fossil carbon by international agreements and governmental actions.**

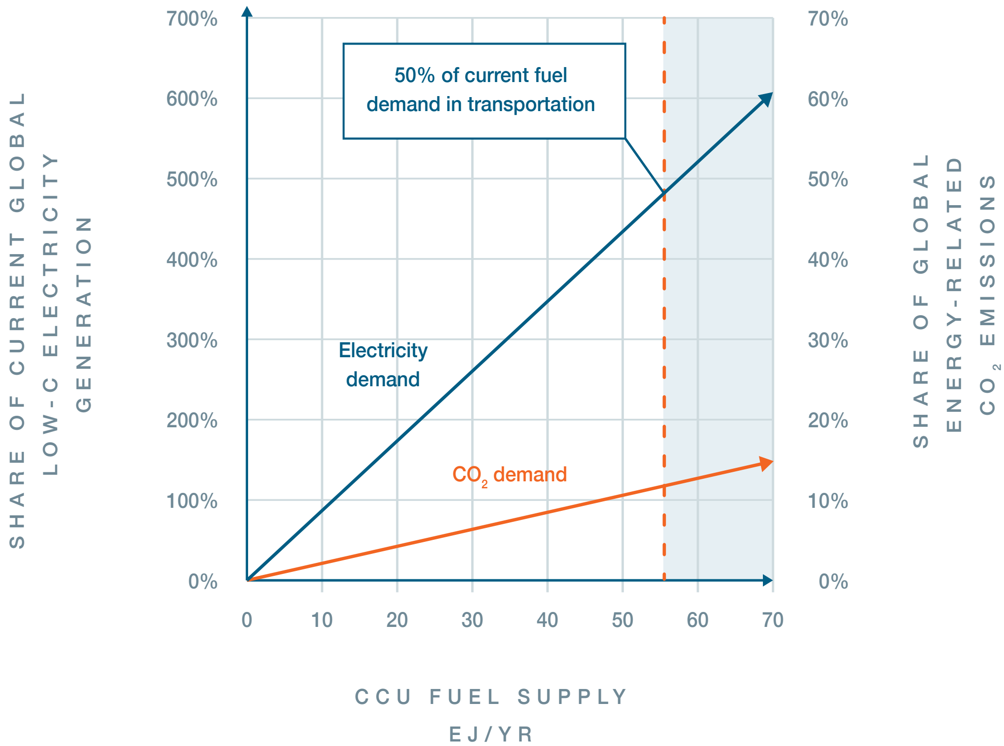

Figure 16. Indicative requirements for electricity and CO_2 at different CCU fuel supply levels illustrated in relation to combined global generation of nuclear and renewable electricity, and global energy related CO_2 emissions in 2012.

4. From centralised to decentralised CO_2 emission sources and the cost of CCU

The tendency to transform our industrial and energy systems towards more distributed production would also mean that CO_2 is emitted from small distributed point sources and thus also increase the costs of CCU plants (e.g. unit costs of captured CO_2). **Solution: Utilisation of a high share of significant industrial point sources and direct air capture.**

5. Sustainability concerns

Life-cycle assessment methodologies are only just being established for different applications of carbon reuse, and questions like whether fossil CO_2 could be used as raw material alongside biogenic and atmospheric CO_2 are being debated. Reaching consensus on sustainable practices is likely to take time and will possibly delay technology scale-up. **Solution: Standardisation of life-cycle assessment methodologies driven by global intergovernmental organisations.**

6. Competition with other energy carriers

In addition to carbon reuse there are also other pathways to mitigate climate change and replace the use of fossil fuels. As an example, in the carbon reuse economy the cost issues of hydrogen might create challenges compared with other pathways to carbon neutrality. **Solution: Start the utilisation of the carbon reuse economy in applications with high-value products and profitability.**

7. Need for industrial renewal

Decarbonisation of the industrial and transport sectors will be an enormous task and will take decades to accomplish. For example, fossil raw materials are not only used for producing energy and fuels but also as raw materials in today's chemical and steel industries. A total renewal of heavy industry and transport is needed to meet the climate change mitigation targets.

6

CONCLUDING REMARKS

WE HAVE DEMONSTRATED some feasible pathways from carbon dioxide to fuels, chemicals, materials and food. The readiness levels of many of these technologies are relatively high, and in recent years companies have become increasingly interested in CCU technologies. Despite relatively high technological readiness, further development is still needed to improve the efficiency and product portfolios of many CCU processes in order to develop viable business cases. Furthermore, higher-value CCU products are more likely to be commercialised first from a pure business-driver point of view. However, the most important actions to be taken are related to business and the political environment. Commercialisation of the carbon reuse economy requires low carbon energy investments and policies to promote these investments. Moreover, the commercialisation of lower-value products can be accelerated by legislative actions. For example, the new Renewable Energy (RED II) Directive may open up the market for electrofuels in Europe, though its requirements of renewable energy sources needed for electrofuel production are quite strict. Despite the remaining barriers to the commercialisation of CCU, we believe that the carbon reuse economy can have a significant role in mitigating climate change and creating new business based on sustainable carbon.

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