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Green carbon and the chemical industry of the future

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The pressing need to mitigate climate change and drastically reduce environmental pollution and loss of biodiversity has precipitated a so-called energy transition aimed at the decarbonization of energy and defossilization of the chemical industry. The goal is a carbon-neutral (net-zero) society driven by sustainable energy and a circular bio-based economy relying on renewable biomass as the raw material. It will involve the use of green carbon, defined as carbon derived from terrestrial or aquatic biomass or organic waste, including carbon dioxide and methane emissions. It will also necessitate the accompanying use of green hydrogen that is generated by electrolysis of water using a sustainable source of energy, e.g. solar, wind or nuclear. Ninety per cent of the industrial chemicals produced in oil refineries are industrial monomers that constitute the precursors of a large variety of polymers, many of which are plastics. Primary examples of the latter are polyolefins such as polyethylene, polypropylene, polyvinyl chloride and polystyrene. Polyolefins are extremely difficult to recycle back to the olefin monomers and discarded polyolefin plastics generally end up as the plastic waste that is responsible for the degradation of our natural habitat. By contrast, waste biomass, such as the lignocellulose contained in forestry residues and agricultural waste, constitutes a renewable feedstock for the sustainable production of industrial monomers and the corresponding polymers. The latter could be the same polyolefins that are currently produced in oil refineries but a more attractive long-term alternative is to produce polyesters and polyamides that can be recycled back to the original monomers: a paradigm shift to a truly bio-based circular economy on the road to a net-zero chemical industry.

This article is part of the discussion meeting issue 'Green carbon for the chemical industry of the future'.

1. Introduction

There is mounting global support for the mitigation of climate change by drastically reducing the carbon footprint of chemicals manufacture and eliminating the vast environmental pollution resulting from the massive amounts of waste generated, directly or indirectly, by the chemical and allied industries. This forms the prime motivation for a paradigm shift to a carbon neutral, circular economy [1,2]. In order to maintain global warming below the 1.5°C specified in the Paris Agreement, all anthropogenic CO_2 emissions will need to reach net zero by mid-century. The chemical industry accounts for *ca* 2 billion tonnes of CO_2 emissions per annum, which corresponds to 5% of total greenhouse gas (GHG) emissions [3]. In order to achieve the net-zero goal, the chemical industry must undergo a complete metamorphosis to emerge as a truly sustainable carbo-chemical industry [4,5]. The linear flow of materials that pervades the twentieth century consumer society is not appropriate for addressing the ecological challenges that society currently faces.

The root cause of these ecological problems is waste, in its many manifestations [6]. It includes the prodigious amounts of CO_2 generated as waste by the processing of fossil resources, waste from plastics used for packaging, food supply chain waste (FSCW) and industrial waste produced by the chemical and allied industries such as steel and cement manufacture (see figure 1).

2. The worldwide chemical industry

Chemicals manufacture has always been based on raw materials produced as waste from other industries. In the mid-nineteenth century coal was used to provide the energy needed to drive the wheels of the industrial revolution. In 1856, W. H. Perkin, in an attempt to synthesize quinine for the treatment of malaria, by oxidation of toluidine with potassium dichromate, serendipitously invented the synthetic dye, mauveine [7]. Toluidine is a constituent of coal-tar, a waste material derived from the use of coal as an energy source, and this monumental invention formed the basis for a chemical industry based on coal tar as the basic raw material.

The first petrochemicals, ethylene and propylene, were produced in West Virginia, USA, in 1921 by thermal cracking of ethane and propane, waste products of petroleum (oil) refining [8]. This marked the advent of the petrochemical industry as a spin-off of oil refining for the production of liquid fuels. It subsequently led in the 1930–1950s, to a flourishing petrochemical industry based on lower olefins and aromatics, the by-products of oil refining for transportation fuels. The industry had its heyday in the 1960s and 1970s but suffered a serious hiccup in October 1973 when the Arab members of the Organisation of Petroleum Exporting Countries imposed an oil embargo on countries—the United States, United Kingdom, Canada, Japan and The Netherlands (and later South Africa)—that had supported Israel during the Arab–Israeli conflict in 1973. It resulted in an immediate increase in the price of crude oil, from $2.90 to $11.65 per barrel in January 1974.

Although the embargo was lifted in March 1974, the first 'oil crisis' sent shock waves through the global oil industry, with long-term effects on geopolitics and the global economy.

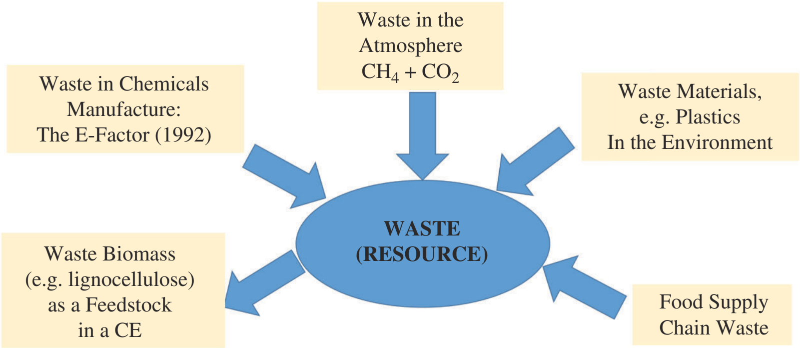


Figure 1. The ubiquity of waste.

It sent a particular message to the major oil companies worldwide. The message was this: we better start thinking about how we will produce commodity chemicals and liquid fuels if we have no or limited access to crude oil as the feedstock?

The technical solution was waiting in the wings. Coal was still an inexpensive, readily available and popular raw material back in 1974 when there was no talk of a road to carbon neutrality despite the Limits to Growth Report of the Club of Rome published in 1972 [9] and the UN Conference on the Human Environment, held in Stockholm in the same year [10], which was the first conference to mention climate change. Coal is a solid and more difficult to process than a liquid such as crude oil. On the other hand, coal gasification processes were already known at the time. Hence, the oil crisis led to renewed interest in chemicals from coal, especially because the oil to coal price ratio had dramatically increased as a result of the oil crisis. Moreover, it was also acknowledged that coal could be replaced by any biomass as the feedstock [11].

There were basically two technologies for converting coal to liquid hydrocarbons: hydrogenation (Bergius process) and gasification to a mixture of carbon monoxide and hydrogen, known as syngas, followed by the Fischer–Tropsch process to convert the syngas to hydrocarbon fuels (figure 2). Similarly, bulk chemicals could be produced from syngas but it was recognized that if transport from remote locations was needed, the syngas could be first converted to methanol, which could be easily transported to the desired location where, if necessary, it is converted back to syngas or processed further as in Olah's methanol economy [12]. Oil-based petrochemicals manufacture in oil refineries is still the underpinning technology but it is coming under increasing pressure to change in the envisaged decarbonization of the energy sector and defossilization of chemicals manufacture on the road to sustainable chemicals manufacture with net-zero GHG emissions.

Currently, *ca* 400 million tonnes per annum of lower olefins and aromatics (base chemicals) are produced from fossil feedstocks: oil, coal and natural gas. Roughly, 90% of these base chemicals are further converted to a wide variety of polymers, most of which are plastics. One could say therefore, that the petrochemical industry is primarily a plastics industry using lower olefins and aromatics, derived from fossil resources, as the major feedstocks. This situation is not sustainable in the current drive to reduce GHG emissions and plastic waste in the environment that are the root causes of climate change and environmental degradation, respectively.

What has changed in the last 50 years with regard to the challenges and the possible solutions?

Challenges:

- Climate change: the road to net zero
- The decarbonization of energy: coal no longer a viable option
- The defossilization of chemicals manufacture

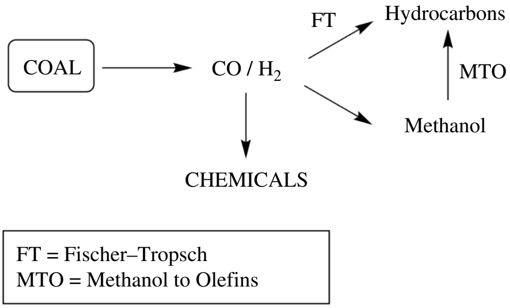


Figure 2. Conversion of coal to commodity chemicals via syngas.

- The plastic pollution challenge

Solutions:

- Sustainable electricity from wind, solar and nuclear energy
- The circular bio-based economy
- Chemicals from renewable biomass
- The ascendance of biocatalysis as an enabling sustainable technology

With regard to technical solutions the influence of biocatalysis cannot be overestimated. As a result of spectacular developments in protein engineering and directed evolution, underpinned by advances in (meta)genomics and bio-informatics, the scope and power of both whole cell and cell-free biocatalysis have made it the method of choice for a variety of transformations. Syngas fermentation to directly afford a variety of commodity chemicals, for example, was not on the agenda 50 years ago. Enzymatic recycling of polyethylene tetraphthalate (PET) and related polyester plastics is rapidly becoming a viable solution to the plastic pollution problem caused by these polymers (see later). What is clearly needed, therefore, is a transformation to a Circular Carbo-Chemical Industry (Waste to Wealth) based on a renewable feedstock and resulting in a drastic reduction in waste plastics. Indeed, the valorization of waste biomass is at the very heart of the bio-based economy.

3. Waste in the chemical industry: the E-Factor and beyond

In 1992, we introduced the E(nvironmental)-Factor that drew attention to the enormous amounts of waste generated in the production of fine chemicals and pharmaceuticals [13]. The E-Factor was defined as ‘everything but the desired product’, including, by definition, carbon dioxide formed as a by-product of energy usage. The enormous amounts of waste could be largely attributed to the widespread use of reactions, such as reductions and oxidations, involving stoichiometric amounts of mainly inorganic reagents. The solution was clear: replace such antiquated stoichiometric methodologies with greener, catalytic alternatives, such as catalytic hydrogenation and catalytic oxidations with dioxygen or hydrogen peroxide. This was not only limited to fine chemicals and pharmaceuticals. In some cases, the production of industrial monomers for bulk polymers afforded substantial amounts of inorganic salts as waste. Prominent examples included 3 kg of calcium chloride per kg of propylene oxide and 4.5 kg of ammonium sulfate per kg of caprolactam [14]. In the meantime, these processes have been largely displaced by cleaner catalytic alternatives.

The E-Factor also included waste, expressed as kg of CO_2, generated from the energy consumption in the process but the data were generally not widely available in 1992. However, the currently envisaged energy transition to net zero necessitates a decarbonization of the energy sector and a defossilization of chemicals manufacture. In this scenario, the carbon

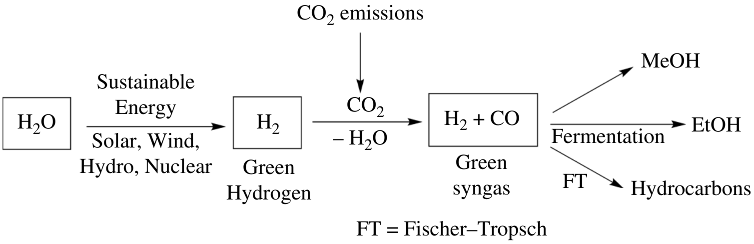


Figure 3. Chemicals from carbon dioxide, water and sustainable energy.

footprints of products are continually increasing and the amounts of CO_2 generated have become part of the equation. Relevant numbers include [4]:

- The organic chemical industry accounts for *ca* 5% of global CO_2 emissions.
- Base chemicals production accounts for 1–2.5 kg CO_2/kg product.
- Plastics production accounts for 2.5 kg CO_2/kg product, which becomes 5 kg CO_2/kg product when use and disposal are included.
- Co-production of 5–10 kg inorganic waste in the whole chain of some plastics production.

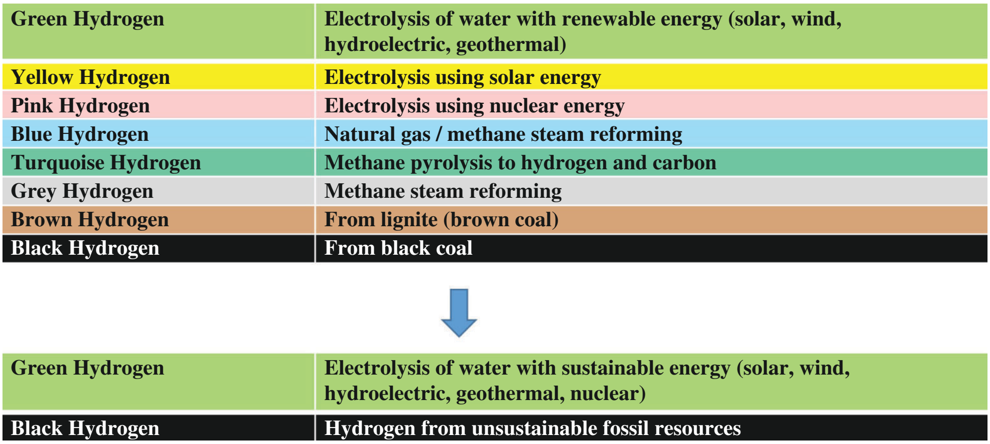
4. The chemical industry of the future

It is important to note [4] that in the near future, as a result of extensive decarbonization of the energy sector, there is more likely to be an excess rather than a shortage of fossil resources for chemicals production. Taken together with the expectation that defossilization will likely be a slow process, this means that there will very likely be an excess of fossil feedstocks that the petrochemical companies will mobilize for chemicals manufacture. However, from the point of view of continuity, it makes more sense to transform the industry into chemicals production based on green hydrogen, generated by electrolysis of water or valorization of waste, e.g. waste plastics [15] using a sustainable source of electricity [16] and a source of green carbon or carbon waste, e.g. carbon dioxide (figure 3) or waste plastic.

First, we need to clearly define what we mean by green hydrogen and green carbon. A whole rainbow of colours is currently used to distinguish between the different origins of the carbon and hydrogen. The hydrogen rainbow is shown in figure 4 [17]. Green hydrogen is hydrogen produced by electrolysis of water using green electrons from a sustainable source of energy. The latter is currently viewed as being solar, wind, hydroelectric or geothermal energy. Hydrogen produced using solar energy is also designated as yellow hydrogen which would seem to be superfluous.

Hydrogen produced using nuclear energy is designated as pink hydrogen. However, there are convincing arguments for considering nuclear energy to be sustainable and green [18]. In the energy option, ‘sustainable’ implies the ability to supply energy for indefinitely long periods on a timescale spanning civilizations without depriving future generations and in a way that is environmentally friendly, safe, reliable and economically viable. This is particularly the case with modern fast-neutron uranium fission reactors. In the longer term, thorium molten salt fast reactors could be an even more attractive proposition [19]. Another recent development that could benefit the use of nuclear energy in chemical manufacturing facilities is the use of small modular reactors that deliver low carbon energy at a reasonable price [20].

The carbon rainbow is shown in figure 5 [21]. In this scenario, the term green carbon is currently restricted to carbon from terrestrial plants. Carbon stored in ocean plants and sediments is regarded as blue carbon and carbon stored in fresh water and wetlands as teal carbon. Red carbon is reserved for carbon released through biological particles on snow. Purple and grey carbon are carbon captured from air or industrial emissions and carbon released



Green Hydrogen	**Electrolysis of water with renewable energy (solar, wind, hydroelectric, geothermal)**
Yellow Hydrogen	**Electrolysis using solar energy**
Pink Hydrogen	**Electrolysis using nuclear energy**
Blue Hydrogen	**Natural gas / methane steam reforming**
Turquoise Hydrogen	**Methane pyrolysis to hydrogen and carbon**
Grey Hydrogen	**Methane steam reforming**
Brown Hydrogen	**From lignite (brown coal)**
Black Hydrogen	**From black coal**

Green Hydrogen	**Electrolysis of water with sustainable energy (solar, wind, hydroelectric, geothermal, nuclear)**
Black Hydrogen	**Hydrogen from unsustainable fossil resources**

Figure 4. The hydrogen rainbow.

through industrial emissions. Brown carbon is carbon released by incomplete combustion of organic matter. We propose that this be simplified to: green carbon is carbon stored in terrestrial, ocean and freshwater plants and algae. Brown carbon is carbon from industrial emissions and combustion of fossil resources.

5. Chemicals from biomass valorization: the bio-based circular economy

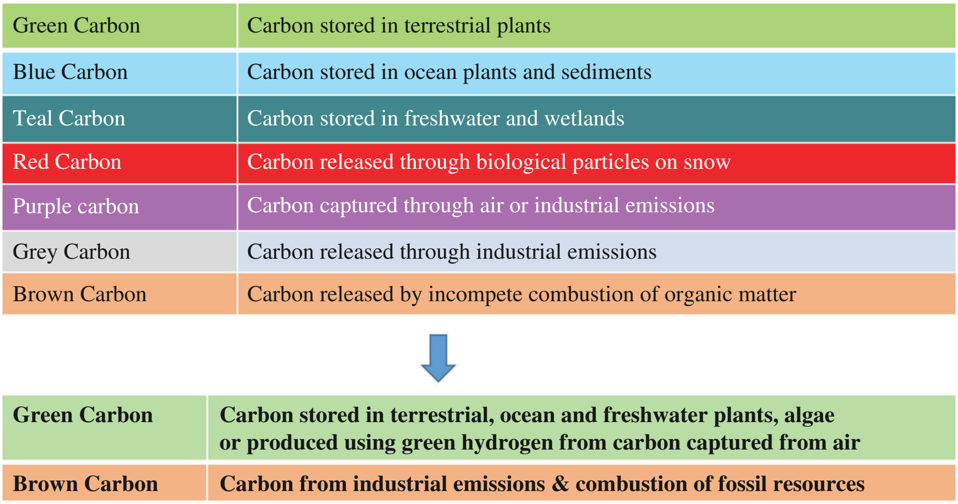
By analogy with the production of chemicals and liquid fuels from coal envisaged in the 1970s, lignocellulosic waste can be chemo-catalytically converted to the same products (figure 6) via gasification to syngas followed by methanol synthesis or Fischer–Tropsch conversion to hydrocarbons [22,23]. Alternatively, fermentation of syngas using acetogenic bacteria produces essentially the same pallet of products as that produced by the fermentation of glucose [24]. It has also been integrated with microbial electrosynthesis (MES) in the production of acetic acid [25].

Waste lignocellulosic biomass also provides a range of monomers and polymers that have the potential to replace petrochemical-based materials in a wide range of applications [26]. For example, hydrolytic conversion (saccharification) of lignocellulose affords C_6 and C_5 monosaccharides, e.g. glucose and xylose, that are subsequently fermented to ethanol, and a variety of other alcohols, diols and dicarboxylic acids for use as industrial monomers [27]. Indeed, defossilization of chemicals manufacture, by switching to a Circular Carbo-Chemical Industry based on waste biomass as feedstock (Waste to Wealth), that is regenerative by design [28], is the quintessence of the bio-based economy.

In a circular economy, natural resources are preserved and waste is reduced or, better still, eliminated by designing products for recycling and reuse. It corresponds with the concept of sustainable development, which requires that a technology fulfil two conditions: (i) the rate of consumption of natural resources should not deplete supplies over the long term and (ii) the rate of residue generation should be no higher than the natural environment can readily assimilate [29,30]. As the iconic Barry Commoner already remarked in 1971:

> ‘Here is the great fault of the life of man in the ecosphere [31]. We have broken out of the circle of life, converting its endless cycles into man-made linear events: oil is taken from the ground, distilled into fuel, burned in an engine, converted thereby into noxious fumes which are emitted in the air.’

Currently, the bio-based economy is based almost exclusively on first generation (1G) feedstocks consisting primarily of corn and cassava starch, sugar cane and sugar beet and



Green Carbon	Carbon stored in terrestrial plants
Blue Carbon	Carbon stored in ocean plants and sediments
Teal Carbon	Carbon stored in freshwater and wetlands
Red Carbon	Carbon released through biological particles on snow
Purple carbon	Carbon captured through air or industrial emissions
Grey Carbon	Carbon released through industrial emissions
Brown Carbon	Carbon released by incompete combustion of organic matter

Green Carbon	**Carbon stored in terrestrial, ocean and freshwater plants, algae or produced using green hydrogen from carbon captured from air**
Brown Carbon	**Carbon from industrial emissions & combustion of fossil resources**

Figure 5. The carbon rainbow.

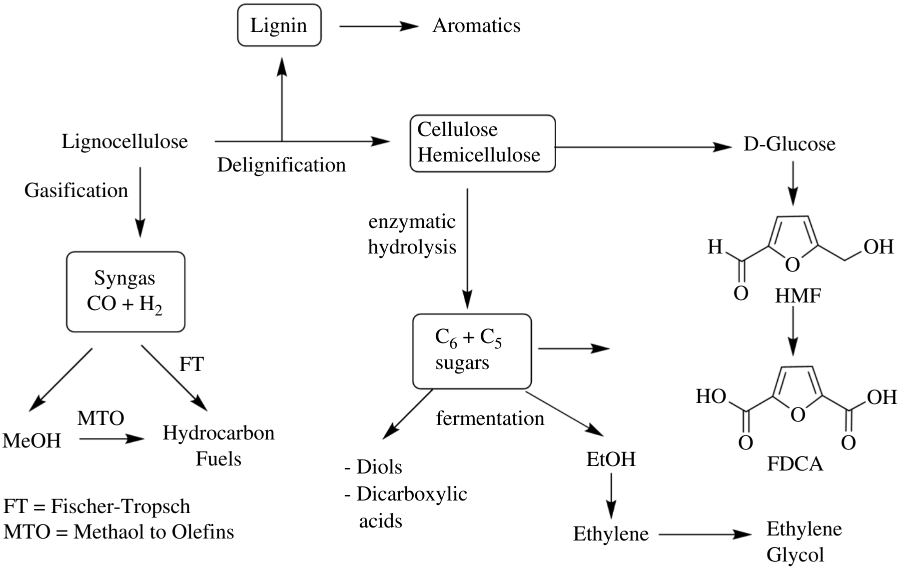


Figure 6. Conversion of lignocellulose to chemicals and biofuels.

triglycerides from vegetable oils such as rape seed oil. However, their use as feedstocks for chemicals manufacture is not perceived as sustainable in the longer term because of competition, directly or indirectly, with food production. By contrast, second generation (2G) biomass feedstocks, comprising lignocellulose, hemicellulose, pectin and chitin, are not used in food production. In addition, various aquatic polysaccharides from micro- and macro-algae, that differ structurally from terrestrial counterparts, are potential feedstocks for third generation (3G) biorefineries [32,33].

Lignocellulosic waste contained in agricultural and forestry residues, constitutes a suitable feedstock for valorization to commodity chemicals in integrated biorefineries [34,35]. It is generated, in the form of sugar cane bagasse, sugar beet pulp, cassava pulp [36], corn stover, wheat straw and rice straw, in hundreds of millions of tonnes per annum [37], far exceeding the annual global production of the major petrochemicals, ethylene (150 million tonnes), propylene (90 million tonnes) and para-xylene (40 million tonnes). Valorization of this waste is at the heart of a bio-based circular economy [38–40]. Similarly, *ca* 1.3 billion tonnes per annum [41] of FSCW, corresponding to *ca* 30% of total food production [42–44], can be converted to value-added products.

Historically, the goal of lignocellulose biorefining was to produce high-quality cellulose for paper manufacture. However, the harsh conditions resulted in irreversible degradation of the lignin to an intractable material that is only suitable for use as an inexpensive energy source. By contrast, it is now acknowledged that economic viability depends on the valorization all three components of lignocellulose, that is cellulose (35–50%), hemicellulose (20–35%) and lignin (10–25%). Lignin is potentially an important source of renewable aromatic building blocks. This led to the design of 'lignin first' pretreatment concepts [45,46] that rely on the stabilization of reactive lignin intermediates during lignocellulose fractionation.

(a) Bio-based building blocks and polymers

The motivation for switching to bio-based plastics is to reduce CO_2 emissions but their facile recyclability and biodegradability can also be valuable assets. Bio-based polymers are divided into two categories: drop-in replacements and new bio-based polymers [47]. The former are chemically identical to their petrochemical counterparts but are, at least partially, produced from renewable biomass. Examples include polyethylene (PE) from bioethanol and PET from bioethylene glycol. The overall market leader is drop-in bio-based PET with a 20% bio-based carbon content, derived from bioethanol (2 C atoms) and fossil-derived p-xylene (8 C atoms). Currently, much research effort is devoted to the synthesis of bio-based terephthalic acid, which would enable the production of 100% bio-based PET.

On the other hand, PET could be substituted with polyethylene furandicarboxylate (PEF), a fully bio-based alternative developed by Avantium [48]. PEF is produced from (bio) ethylene glycol and an ester of furan−2,5-dicarboxylic acid (FDCA). The latter is prepared by chemo- [49] or biocatalytic oxidation [50–52], or electro-catalytic oxidation [53,54] of 5-hydroxymethylfurfural (HMF) or 5-chloromethylfurfural (figure 7) [55]. In addition to being 100% bio-based, i.e. carbon neutral, PEF has superior mechanical, thermal and gas barrier properties compared with PET and is processed in the same way and using the same machinery as PET [56,57]. Similarly, a variety of carbon neutral bio-polyesters (see figure 7 for structures), derived from FDCA and bio-based diols, such as 1.3-propane diol and 1,4-butane diol, have been commercialized [58] and the topic has recently been reviewed [59]. The various possibilities for replacing PET by PEF and analogous fully bio-based alternatives formed the subject of a tutorial review [57].

It is also noteworthy that plastic films have been made from natural biopolymers such as starch and chitosan [60,61] and polyhydroxy alkanoates (PHAs; see §5b).

(b) The way forward

As we move towards a circular bio-based economy involving the replacement of fossil hydrocarbon resources (oil and gas) with sustainable polysaccharides from waste biomass, we are substituting low oxidation state hydrocarbons with high oxidation state carbohydrates as feedstocks. On the other hand, *ca* 90% of the products of the petrochemical industry are polymers and the largest group of polymers are the polyolefins, particularly PE and PP. These very same polyolefin plastics are by far the major cause of plastic pollution (see §6) and they cannot be recycled to the original monomers to achieve a circular economy.

Consequently, the business as usual scenario of defossilization that involves conversion of renewable biomass to low-valent olefins, in an update of the 1973 model (see §2), e.g. via syngas or by fermentation of glucose to ethanol and dehydration of the latter to ethylene, is not circular as there is no recycling back to the monomers.

By contrast, bio-based condensation polymers (see figure 8), such as polyesters (e.g. PET and PEF) and polyamides involve monomers, e.g. diesters and diamides, respectively, that are in higher oxidation states than olefins and can be produced by fermentation of sugars. In

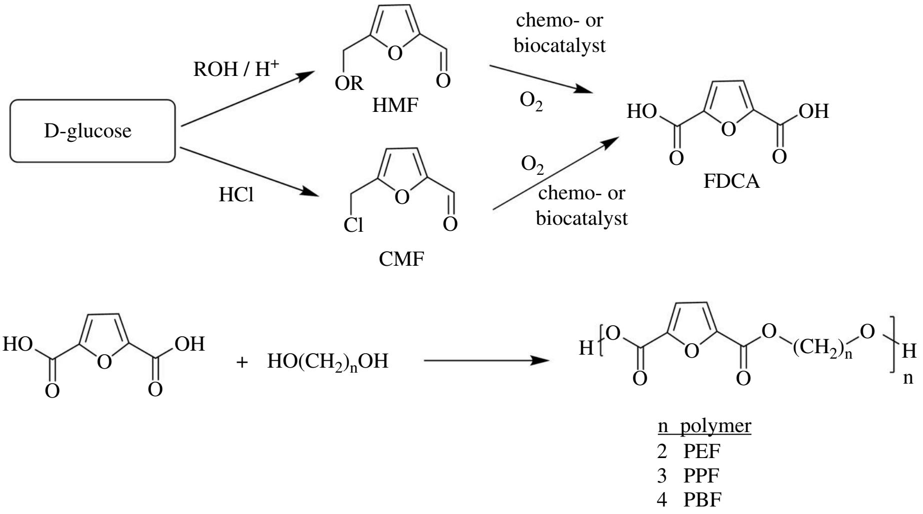


Figure 7. Production of PEF and related polyesters.

contrast to polyolefins, recycling of polyesters and polyamides to the constituent monomers is, in principle, feasible via chemo- or biocatalytic methods. Moreover, in addition to being more easily recycled, bio-based condensation polymers [62,63] are generally safer, and biodegradable [64,65].

The downside is that bio-based condensation polymers are currently more expensive to produce than the polyolefins they seek to replace. It is noteworthy, however, that the cost-price of polyolefins has been optimized over a period of more than 70 years, whereas the corresponding polyesters have not yet reached their optimum cost of goods. However, application of the principle of extended producer responsibility (EPR), whereby the costs of treating and/or disposing of waste are integrated into the cost of goods of plastics, would result, overnight, in a much more favourable cost differential for polyester replacements [66].

What is the conclusion? As we move from an unsustainable polyolefins industry based on oil and gas to a carbon neutral polymer industry based on renewable biomass, we have the chance to combine the envisaged defossilization of the polymer industry with seriously starting the change to a truly sustainable polymer industry based on condensation polymers, such as polyesters and polyamides, that can be recycled back to the original monomers. The substantial progress in the use of metabolic pathway engineering [67,68] to optimize existing biochemical pathways or to develop new pathways for the fermentative production of bio-based monomers such as diols and di-carboxylic acids lends significant support to this change. In short, this is a unique moment in the history of the chemical industry. Can we afford to miss this golden opportunity for designing and implementing this long-awaited transmutation of the plastics industry?

6. The plastic pollution challenge

We cannot imagine a world without plastics today. However, the massive contamination by single-use plastics (SUPs) has a devastating effect on our natural environment. These plastics are produced from fossil-derived hydrocarbons, notably ethylene, propylene and aromatics. The largest volume non-fibre plastics are PE (36%), polypropylene, PP (21%) and polyvinyl chloride (12%), followed by PET, polystyrene (PS) and polyurethanes. Together, these seven products account for 92% of all the polymers that were ever made. Polyesters, particularly PET, account for most of the fibre production. Single-use applications in packaging, primarily involving PE, PP and PET, involves 42% of all non-fibre plastics.

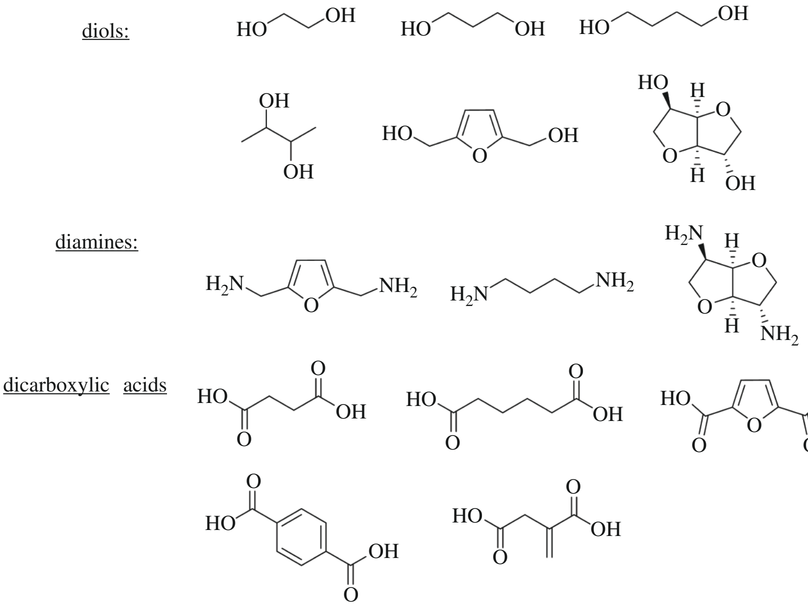


Figure 8. Bio-based monomers for polyesters and polyamides.

In the period 1950–2015, the cumulative generation of primary and secondary (recycled) plastic waste amounted to 6300 million tonnes [69], of which *ca* 800 million tonnes (12%) was incinerated and 600 million tonnes (9%) was recycled. Roughly, 4900 million tonnes, i.e. 60% of all the plastics ever made, were discarded and accumulated in landfills or in the natural environment. Clearly, single-use application of non-biodegradable plastics is unsustainable and must be replaced by a circular economy in which plastics are designed for recyclability. None of these currently used plastics biodegrade in the natural environment but sunlight can cause their fragmentation into microplastics (50 µm–5 mm) [70] or nanoplastics (less than 0.1 µm) [71], the long-term environmental impact of which is largely unknown.

(a) Enzymatic synthesis of (bio-based) polyesters and polyamides

The sustainability of polymers is also enhanced by using green enzymatic methods for their production. This is not feasible with polyolefins, but polyesters [72–74] and polyamides [75] are amenable to enzymatic production. Polybutylene succinate (PBS), for example, is biodegradable and produced from raw materials—1,4-butane diol and succinic acid—that are derived from renewable biomass. Applications, in biodegradable thermoplastics, require a high-molecular weight (>20 000) polymer, the production of which requires the use of organometallic catalysts at elevated temperatures (>190°C). This results in discoloration and difficult removal of residual amounts of metals from the polymer. By contrast, PBS with a molecular weight of 38 000 was produced by polymerization of diethyl succinate with 1.4-butane diol catalysed by the well-known lipase, Nov435, at 95°C in diphenyl ether as solvent [76] to create a single liquid phase.

Bio-based polyesters and polyamides can be produced by Nov435 catalysed reaction of FDCA esters with diols [11] or diamines [77]. Similarly, the diol produced by hydrogenation of HMF (2,5-bis-hydroxymethylfuran (BHMF)) can be converted to polyesters by Nov435 catalysed polymerization with esters of dicarboxylic acids, including FDCA (figure 9).

Lactic acid is a prime example of a commodity chemical produced by fermentation and polylactic acid (PLA) is 100% bio-based. It is also biodegradable but only under certain conditions, i.e. strictly speaking, it is industrially compostable. It is the most well-established

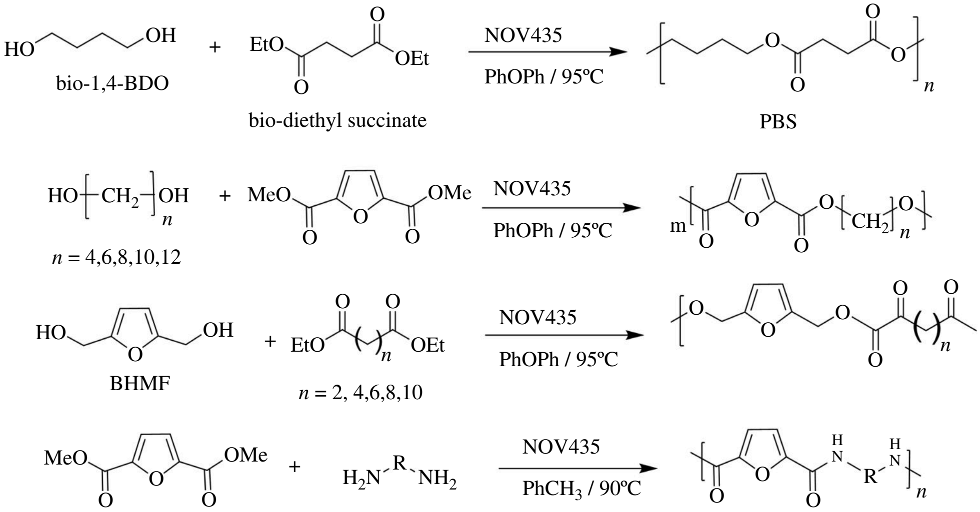


Figure 9. Nov435 catalysed synthesis of biobased polyesters and polyamides.

bio-based polymer with a production of 195 000 tonnes per annum in 2015 and is expected to grow substantially in the future [78].

The structurally similar PHAs are examples of new bio-based polymers that are biodegradable, even in cold sea water (figure 10). PHAs are responsible for energy and carbon storage in certain species of acetogenic bacteria, such as *Plasticicumulans acidivorans*, and can comprise up to 90% of the dry weight of the microorganism [79]. Whereas industrial monomers can be produced from waste lignocellulose, PHAs can be produced directly from any organic waste, such as FSCW [80] or even waste plastics such as PS [81]. Some PHAs are suitable for producing plastic films and are potential replacements for polyolefins as SUPs in packaging but the current high cost of goods is a serious obstacle. This scenario would change drastically by application of EPR. A recent review of the environmental impact of bio-based plastics [82] concluded that substitution of two-thirds of the global plastics demand with bio-based alternatives would deliver an annual reduction of 241–316 million tonnes of CO_2 equivalents.

7. E-biorefineries: electrons as reagents

In the chemical industry of the future, sustainable, green electricity will be used to convert waste carbon—as CO_2 (or methane) or waste biomass—into commodity chemicals and corresponding downstream polymers in e-biorefineries [83–85]. As discussed in §4, green hydrogen, derived from water electrolysis, can be used in the catalytic hydrogenation of CO_2 to syngas and be followed by further conversion to chemicals and liquid fuels. However, in an e-biorefinery, the hydrogen and the CO could be coproduced by electrolysis of a mixture of water and CO_2. This could involve concurrent generation of CO and H_2 in the same electrolyser cell or separated generation of CO and H_2 in two different electrolysers. Raya-Imbernon *et al.* [86] compared these two approaches, using a combination of experimental data and techno-economic analysis, and came to the conclusion that the most economical way of producing syngas is by operating a CO_2 electrolyser with the goal of producing only CO as the final product and then coupling it to a polymer electrolyte membrane electrolyser for H_2 supply. Since many industries rely on a consistent supply of syngas, the electrochemical reduction of CO_2 and water to syngas can contribute to their transformation to become more sustainable and eventually carbon negative [87].

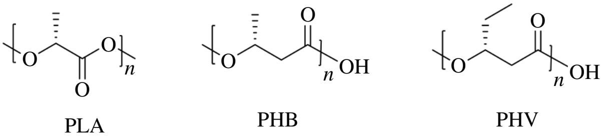


Figure 10. PLA and PHAs.

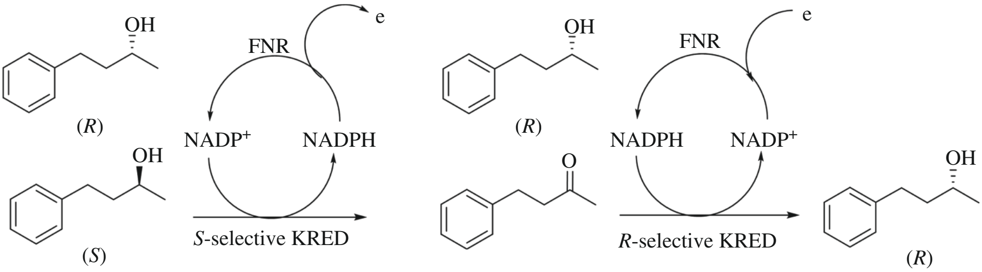


Figure 11. Electrobiocatalytic deracemization of a secondary alcohol.

(a) The renaissance of organic electrosynthesis

Future scenarios with widespread availability of sustainable electricity have led to a veritable renaissance in organic electrosynthesis as an environmentally friendly methodology in which electrons serve as green and sustainable reagents to replace stoichiometric oxidants and reductants with low waste and correspondingly low E-Factors [88]. A prominent example is the use of the well-known aminoxyl radicals TEMPO or derivatives thereof, such as 4-acetamido-TEMPO, as catalysts in the electrocatalytic oxidation of alcohols [89]. In particular, in the context of renewable biomass conversion, water soluble biomass-derived hexose and pentose building blocks and their downstream products are particularly interesting substrates for such electrocatalytic oxidations. For example, 5-HMF (see earlier) was efficiently converted under mild conditions, to either 2,5-FDCA or 2,5-BHMF, using a carbon-supported silver catalyst (Ag/C) as the cathode catalyst together with the homogeneous 4-acetamido-TEMPO, and an inexpensive carbon felt electrode. The insensitivity of the oxidation to anode potential made it feasible to conduct HMF reduction to BHMF at the cathode and oxidation to FDCA at the anode, in a single divided cell operated under cathode potential control, to achieve high yields of BHMF (85%) and FDCA (98%) and a combined electron efficiency of 187% [90]. Another interesting possibility is *in situ* electrolytic generation of hydrogen peroxide [91], which can then be used for selective oxidation of a variety of substrates.

(b) Electrobiocatalysis

Sustainable electricity can also be utilized to drive biocatalytic processes involving whole-cell or cell-free biocatalysis. An example of the former is MES in which the electricity is coupled to the carbon and energy metabolism of electroactive acetogenic bacteria that mediate the conversion of a mixture of CO_2 and water to acetic acid, ethanol, formate and methanol [92,93]. The production of bio-based acetic acid using acetogenic bacteria could provide a commercially viable route for producing acetic acid from carbon capture CO_2 (carbon capture and utilization (CCU)) [94]. The initial product mixture obtained by MES can also be converted further by electrofermentation [95,96]. An intriguing possibility is direct production of PHAs by reduction of CO_2 to short-chain fatty acids that are further converted by PHA accumulating microorganisms [97]. Electrobiocatalysis with free enzymes involves the electrochemical regeneration of redox cofactors such as NAD(P)/NAD(P)H catalysed in enzymatic reductions and oxidations as an alternative for using a second enzyme and a co-substrate. An elegant example is provided by the one-pot, two-electrode deracemization of chiral secondary alcohols (figure 11) reported by Turner *et al*. [98].

8. Conclusions and outlook

The chemical industry of the future will be very much influenced and shaped by the ongoing transition involving the decarbonization of the energy sector and the defossilization of chemicals manufacture. This transition is necessary in order to mitigate climate change resulting from fossil resource-derived waste carbon dioxide and other GHGs and to combat other major sources of waste such as that caused by SUPs. Decarbonization of the energy sector will involve switching from the use of fossil resource-derived oil, coal and natural gas to the use of sustainable electricity, from solar, wind, hydro and nuclear, as the energy source for heating, transport and major industries. The (organic) chemical industry will use sustainable electricity for its energy requirements but it will also require a source of green, sustainable carbon as an alternative for fossil resources.

In order to create a circular economy green carbon will be derived from hydrogenation of CO_2 with green hydrogen or electrolytic reduction of CO_2 with water, to afford syngas. Alternatively, the green carbon can be derived from 2G waste lignocellulosic biomass, such as agricultural and forestry residues, by hydrolysis to hexoses and pentoses and subsequent catalytic conversion or fermentation. Ninety per cent (in volume) of the chemicals produced by the (petro)chemical industry are raw materials for polymers and 90% of these polymers are plastics, primarily PE and PP for single use packaging applications. Although these olefins can be produced from sustainable biomass or syngas, by fermentation to ethanol and subsequent dehydration to ethylene, polyolefin plastics are a major source of pollution as SUPs. It could make more sense, therefore, to convert waste CO_2 or lignocellulose or plastic waste to monomers for bio-based plastics or directly by fermentation to PHA plastics in e-biorefineries. Moreover, current and future developments in metagenomics, directed evolution of enzymes and metabolic pathway engineering of whole microbial cells, aided by advances in bioinformatics and machine learning, will enable the development of even more cost-effective biocatalytic conversions.

One might ask the question: How will the biorefineries of the future chemical industry compare with existing refineries, with regard to reactor size, rate of production, location, etc. However, this is difficult to answer as the choice of technology or, rather, technologies still has to be made. One thing is reasonably certain and that is that the feedstock for the carbon of the future will not be fossilized hydrocarbons. It will be either carbon dioxide or waste biomass and, possibly, small amounts of waste polyolefin plastics. As we have shown, there are various possibilities for converting this biomass to commodity chemicals (mostly industrial monomers) and the choice for which possibility still has to be made. As we noted already in the 1970s, the choice will probably be dependent on geographical location. In remote locations, either CO_2 or biomass could be converted into syngas or methanol and the latter transported to, for example, Europe for further conversion. In this case, reactors and processes would be similar to those currently used in South Africa for conversion of syngas to liquid fuels and chemicals. Alternatively, waste polysaccharide biomass can be converted, using chemo- or biocatalysis in liquid phase processes. The choice of technology will also be influenced by the use of green electricity as the energy source. The refineries of the future will largely be e-biorefineries, using electrocatalytic processes, which will also have an important influence on reactor type and size.

In short, the future of a chemical industry based on green carbon looks bright from several viewpoints. Although the contribution of the (organic) chemical industry to CO_2 emissions represents only 5% of the total emissions, the major technical developments on the road to net zero have far reaching implications for industry in general. To cite one of the many examples, the application of CCU to the production of cement, which is responsible for 7% of all CO_2 emissions [99]. In order to end on an optimistic note: if we are prepared to make the effort, perhaps we could even be the first generation to be fully sustainable [100].

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