Supplementary document – bio-based products review

Contents

1. Introduction

This document contains a review of how biomass is or could be used to make various important chemical products such as platform chemicals, plastics and other polymers, solvents, and fine and speciality chemicals. The information it contains was used to support the development of the Supergen Bioenergy Hub and Biomass Biorefinery Network report "Carbon for chemicals: How can biomass contribute to the defossilisation of the chemicals sector?".

This review is not designed to be exhaustive but to act as an introduction and to highlight opportunities. It does not attempt to cover the entire array of products found in the scientific literature. The complexity of the chemicals sector and lack of publicly available data make it hard to get a full and detailed picture of bio-based chemicals production. We have used academic publications as well as a variety of online information sources to carry out this review and interpreted this information to the best of our ability. In particular, it is often not clear from information companies share online whether a product is bio-based, or bio-attributed.

Some of the discussions below refer to product lifetimes. Product lifetimes will be a distribution and though previous publications gave guidance for some applications (e.g., plastics and PLFs), for other applications data is harder to find [3,18,19].

2. Raw materials

The petrochemical industry takes in several fossil chemical inputs including coal and methane, and oil refinery products such as naphtha and ethane. Biomass can be converted into drop-in replacements for some of these raw materials and fed into existing manufacturing processes to create drop-in bio-based or bio-attributed products. The three main examples of this that will be considered here are naphtha, methane, and syngas.

Naphtha is a mixture of hydrocarbons produced from fossil feedstocks. It is converted via cracking or catalytic reforming into many different products that are used in fuel/energy applications and into several of the core platform chemicals for organic chemical production. Bio-naphtha is produced from bio-oils, such as vegetable oils, and waste oils from paper production or cooking, as a by-product of the HVO processes used for transport and aviation fuel production [1-4]. About 150,000 tonnes of bio-naphtha are produced in Europe each year [2]. Bio-naphtha is used in the biomass balance approach in existing petrochemical facilities: INEOS, BASF and others all have bio-attributed products based on the use of bio-naphtha [5, 6]. Bio-naphtha could provide a route to many bio-based chemicals because of its use in primary chemical production.

Bio-propane (another by-product of the HVO process) and bio-diesel could be used as a cracker feedstock for chemicals production. To our knowledge bio-naphtha, bio-propane, and bio-diesel are not yet being used for chemicals production in the UK.

Methane is the major component of natural gas [7]. Most methane is used as a fuel, but it is also used as a feedstock in the chemical industry, mostly via reforming to syngas and then on to methanol and other chemicals. Bio-methane is already produced commercially, although again the main purpose of this is for energy applications. Biogas, a mixture containing methane and carbon dioxide, is produced via the anaerobic digestion (AD) of biomass feedstocks such as wastes, agricultural residues, and some crops. Biogas is cleaned and upgraded to yield bio-methane [1, 8]. The UK already produces significant amounts of biomethane for energy applications: there are over 1,000 operational or planned AD facilities in the UK, both fed on agricultural feedstocks and other wastes [9]. Bio-methane could be converted to chemicals via syngas, but researchers are also developing novel technologies for bio-conversion of bio-methane to chemicals [10].

Syngas (or synthesis gas) is a gaseous mixture of carbon monoxide, carbon dioxide, hydrogen and water produced from fossil feedstocks, for example via coal gasification or methane reforming [7]. Bio-naphtha and bio-methane can also be used as drop-in replacements and converted to syngas, and this is being done commercially through a biomass balance approach [5]. Bio-derived syngas can be produced via thermochemical processing of bio-naphtha or bio-methane, or via biomass gasification [1, 11]. There are now examples of gasification of biomass to syngas and on to products at commercial scale and more are in the pipeline, though often the focus is on fuel production [12, 13]. Syngas is a key platform for producing many important chemicals and bio-syngas or bio-attributed syngas could be used in the same way, but there are also novel bio-technologies for converting syngas into chemicals starting to emerge, such as gas fermentation [7, 14, 15].

3. Primary and platform chemicals

The raw materials going into the chemical industry are converted into primary chemicals. Despite the complexity of the chemicals system, the production of organic chemicals is built around a relatively small number of primary chemicals, with most organic products derived from just ammonia[1], ethylene, methanol, propylene, and BTX aromatics [7, 16]. Derived from these primary chemicals are more platform chemicals, from which thousands of chemicals and materials are produced [7, 16, 17]. Platform chemicals tend to be produced in large volumes, in a relatively small number of large facilities, and have lower value than more specialised products further down the value chain. Biomass can be used to produce drop-in replacements for existing platform chemicals or intermediates that can be used in the same industry and processes as the fossil counterfactuals they replace. Biomass conversion into the key primary chemicals and their derivatives are explored below.

3.1 Ethylene

Ethylene is an important primary chemical and is the highest volume production organic compound in the chemical industry with global ethylene demand at 161 Mt in 2019 [18, 19]. Almost all ethylene is produced from naphtha or ethane [7]. Some ethylene is also be produced from methanol [7].

The main use for ethylene is the production of its simplest derivative, polyethylene. Polyethylene is a plastic used in several applications but over half is used in short lifetime packaging [7]. Other

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[1] Ammonia is an inorganic nitrogen-based molecule that is made using hydrogen derived from fossil feedstocks. Ammonia is a petrochemical and is used in the production of many organic chemicals but it is not discussed in detail in this report because it is not a carbon-based molecule.

major derivatives include ethylene oxide (used to make ethylene glycol and important in the manufacturing of non-ionic surfactants that are used in products such as home and personal care and pharmaceuticals), ethylene glycol (used to produce polyesters and in a number of non-durable consumer products like anti-freeze), and vinyl chloride (used to make PVC), and styrene (made via reaction with benzene and used in the production of rubbers, resins and plastics such as polystyrene) [1, 7, 20-24].

In the petrochemical industry ethanol is produced from ethylene and used as a solvent and an intermediate. Bioethanol is produced in very large quantities globally, mainly for use as a fuel [1]. It has also drawn much attention as a promising route for biomass to enter the chemical industry due to the possibility to convert it to ethylene. If ethanol demand for fuel falls in the future due to the expected transition to electric vehicles, the chemical industry may be able to tap into the significant bioethanol production capacity that already exists. Most bioethanol production is based on fermentation of sugars from first generation feedstocks such as corn and sugarcane, with the highest volumes coming out of Brazil and the USA [1, 25]. Ethanol from lignocellulosic biomass is less well established, but there is a drive to transition to more lignocellulosic ethanol production due to potential to improve carbon and wider environmental performance and avoided use of food crops. Lignocellulosic ethanol is now becoming a commercial reality with sites operating in Europe and the Americas [26-28]. Routes to ethanol production from bio-syngas are also emerging [12, 29].

Bioethylene is produced at commercial scale via dehydration of bioethanol, and bio-attributed ethylene is produced using bio-naphtha [1, 7, 30-32]. However, bio-ethylene still makes up a small proportion of the ethylene market. In 2019 a JRC report found that there was no significant production of bioethylene in Europe [33]. Several of the key ethylene derivatives are now available in bio-based forms produced from bio-ethylene, for example bio-ethylene oxide and bio-polyethylene, and more are available in bio-attributed forms via bio-attributed ethylene [1, 15, 30, 34-48]. Smart drop-in routes to some derivatives are under development, for example commercial production of bio-ethylene glycol directly from wood feedstocks and sugar is on the horizon [49, 50].

3.2 Propylene

Propylene is another example of the group of key platform chemicals known as olefins. Global propylene demand was 114 Mt in 2019 [51]. Most propylene is produced from feedstocks like naphtha or ethane [7]. Some propylene is also produced from methanol [7].

The main derivative of propylene is polypropylene, making up almost two thirds of propylene demand [7]. Other common derivatives of propylene include propylene oxide (used to make polyols for polyurethane production, and as a solvent in things like paints and coatings), propylene glycol (used to make polyester resins used for construction and transport, and as a solvent and coolant), acrylonitrile (used to make acrylamide, a variety of plastics and rubbers, and acrylic polymers for textiles, carbon fibre manufacture, and PLF applications), acrylamide (used to make polyacrylamide polymers used in PLF applications such as home and personal care products, water treatment, and agrochemicals), acrylic acid (used for the production of commodity acrylates for coatings, sealants, adhesives, textiles, polymer additives, and polyacrylics used in plastics and PLFs), acetone (mainly used as a solvent in a large variety of products, but also for intermediates and additive for plastics production), and phenol (used in phenolic resins which plastics and adhesives, or to make additives for plastics production) [1, 7, 52-56].

Bio-attributed propylene derived from bio-naphtha is already available [1]. Some bio-based propylene production has been reported, via dehydrogenation of bio-based propane [57]. Large scale production of bio-based propylene has not yet taken off. Several other approaches to the production of propylene from biomass have been developed but are not yet at commercial scale [1], including conversion of bio-ethanol, bio-methanol, or bio-isopropanol [1, 58, 59]. Several companies looking at routes to propylene via fermentation have put these on hold due to costs [1].

Though several propylene derivatives are now available in bio-attributed forms, few bio-based versions are commercially available [1, 60-62]. Polypropylene is available in bio-attributed and bio-based forms [57]. Smart drop-ins produced via alternative routes are being developed for several chemicals usually derived from propylene, and some such as bio-propylene glycol derived from bio- glycerol not via propylene are commercially available [1, 61, 63-65]. In fact, bio-glycerol which is a by-product of the oleochemical and biodiesel industries can be an alternative starting point to several valuable propylene derivatives [1]. Acetone can be produced directly by fermentation [48, 66].

3.3 Methanol

Methanol is produced from fossil derived, hydrogen rich syngas [1, 7, 17]. Global methanol demand was 98 Mt in 2019 [67]. Methanol is used for fuel applications, but it is also used in the chemical industry [67]. The main uses for methanol in the chemical industry are the production of formaldehyde (used in adhesives and resins (often for construction), insulating foams, textiles, solvents, and preservatives) and production of ethylene and propylene via the methanol-to-olefins process which is increasingly being used in regions where cheap methanol is produced from coal [7, 68-71]. Other important derivatives of methanol include acetic acid (used to make acetic anhydride, vinyl acetate, and ethyl acetate, and other intermediates for production of a variety of polymers), acetic anhydride (a common intermediate for production of pharmaceuticals and dyes, and used to modify natural cellulose fibres for applications as plastics, coatings, photographic films and cigarette filters), ethyl acetate (a solvent), vinyl acetate (used to make polymers with common applications as PLFs for paints and coatings and adhesives) and methyl methacrylate (MMA) (used for polyacrylics, which are used in PLF applications such as home and personal care products and agrochemicals, and plastics with applications in construction, automotives, and consumer goods [7, 35, 52, 69, 72-74]. Some methanol is also used as a solvent. Production of BTX aromatics from methanol is also under development, although not yet commercial [7].

Bio-methanol can be produced from bio-derived syngas using the same or similar technologies that are used for fossil methanol production [68]. Bio-attributed methanol is commercially available and there are also a small number of plants producing methanol from syngas produced via biomass gasification, with more in the pipeline [12, 68, 75, 76]. However, as with bioethanol, a lot of the bio-methanol production to date appears to be driven by interest in fuel applications, for sectors such as marine transport. Currently biomethanol still represents a small proportion of the global methanol market and it is more expensive than fossil-derived methanol [68].

Bio-attributed versions of formaldehyde and other methanol derivatives are available [75, 77]. Bio-based versions of acetic acid and its derivatives are available commercially, but these tend to be produced from ethanol rather than methanol [1, 35, 78-81]. Smart routes to MMA are the focus of much research due to safety, waste, and cost issues with current MMA production methods, but none are yet commercial [82-84]. Bio-based alternatives to formaldehyde have received significant attention due to concern around the risks posed by formaldehyde in consumer products and building materials [85].

3.4 Aromatics

Aromatics compounds are a specific type of chemically stable ring-based molecule. Benzene, toluene and xylene (BTX) are the basic aromatics used by the chemical industry to synthetise other aromatic chemicals [86]. BTX aromatics are mainly produced via cracking or reforming of naphtha and their production is coupled to the production of ethylene and propylene, but new routes to make aromatic from methanol are in development [7, 87]. Benzene demand is the highest of the BTX aromatics [86]. Total BTX demand was 121 Mt in 2020 [88], 53 Mt of which was benzene [89]. The main use of BTX aromatics is plastics production [87]. In fact, PET, polystyrene, and polyurethane account for 61% of total BTX demand [87]. The most common uses of benzene are the production of styrene via reaction with ethylene (styrene is used in the production of rubbers, resins and plastics such as polystyrene), acetone (mainly used as a solvent in a large variety of products, but also for intermediates and additive for plastics production), phenol (used in phenolic resins which plastics and adhesives, or to make additives for plastics production), aniline (used for polyurethane production), and cyclohexane (used to make adipic acid for nylon manufacture) [86, 90-92]. Toluene is mainly used as a solvent and to produce derivatives such as toluene diisocyanate (used for polyurethanes) [86, 87]. Xylene is used to make terephthalic acid (PTA, used to make PET (polyethylene terephthalate) polymers) and phthalic anhydride (used to make pharmaceuticals, plastics, and plasticizers) and is also used as a solvent and a lubricant [86]. Toluene and xylene are also converted into benzene.

Bio-attributed aromatics are commercially available. Routes to bio-based BTX via biomass gasification or pyrolysis are under development, with some reaching demonstration scale production, but none are yet at commercial scale [1, 93, 94]. Researchers are also developing alternative routes to BTX aromatics from novel bio-based platform chemicals, such as bio-based xylene (specifically para xylene, one isomer of xylene) from fermentation derived isobutanol which has been proven at demonstration scale [45, 95, 96]. Methanol to aromatics processes are currently under development.

Some BTX derivatives, including styrene, acetone, phenol, and a variety of polymers, are available in bio-attributed forms [41, 60, 97-99]. Bio-based production of some derivatives has been demonstrated but commercial production will be reliant on successful deployment of bio-based BTX production at scale. Alternative routes to smart drop-ins for a number of aromatics are being investigated. For example, adipic acid production has been the target of much research because production of adipic acid from cyclohexane is a significant source of anthropogenic Nitrous oxide (NOx) emissions [100, 101]. Alternative routes to bio-adipic acid include direct fermentation but in some applications it could also be replaced by a similar compound, succinic acid, which is readily produced from biomass [1, 97, 102].

Lignin is also a promising source of aromatic compounds because it has a unique structure which naturally contains aromatic rings. Researchers are developing approaches for producing a range of drop-in and novel aromatic compounds from lignin but there are a number of technical challenges that must be overcome if this is to become a viable approach [1, 86, 96, 103]. It is likely that this approach will be more feasible for high value aromatics, such as vanillin (a fragrance and flavouring) much of which is currently derived from BTX aromatics.

4. Novel biobased platform chemicals

4.1 Succinic acid

Succinic acid is a dicarboxylic acid. Fossil based-succinic acid is expensive and so production is limited [1, 104]. Smart routes to bio-based succinic acid, usually direct production via fermentation, have been developed [105]. Bio-based succinic acid is commercially available [1, 35, 106]. Global succinic acid production was approximately 70 kt in 2022, and bio-based production accounts for roughly 50% of the markets [107].

Succinic acid is chemically similar to several platform chemicals currently used in the fossil-based chemical industry and so it can be used as a smart route to drop-ins for a range of currently used chemicals. For example, the major use of bio-succinic acid is expected to be the production of 1,4-Butanediol (BDO) which is currently produced from fossil feedstocks by number of routes, including derivation from propylene [105]. BDO is a polyol used in the production of plastics (e.g., polyesters and polyurethanes), fibres (e.g., polyurethane fibres in the form of

Lycra), tetrahydrofuran (THF, an important solvent), and a range of other derivatives such as plasticizers and pharmaceuticals [1, 108]. Bio-BDO is commercially available and bio-based Lycra based on bio-BDO is in the pipeline [1, 109].

Succinic acid could also be used as a replacement for adipic acid in some applications, such as the production of polyesters or polyamides (nylons). Succinic acid has other useful applications and derivatives, such as bio-degradable polymers like (polybutylene succinate) PBS and novel plasticizers [1, 105, 110].

Bio-succinic acid is an example of a smart drop-in because it can be produced from fossil feedstocks but production from biomass has benefits. Currently the market is fairly small and focused on speciality chemicals but because of the range of derivatives in both drop-in and novel applications, the potential market is large [47]. Cost competitiveness with alternative fossil chemicals is a challenge for succinic acid and its derivatives [111].

4.2 Glycerol

Fossil-based glycerol is a derivative of propylene, but this is an example where the bio-based form actually dominates the market [105]. Large amounts of glycerol are produced as by-products of the processes that convert bio-oils into fatty acids and biodiesel [1, 105]. Approximately 100 kt was produced in 2021, mostly from bio-based sources [112].

Glycerol is directly used in personal care products, pharmaceuticals, and foods, and can also be a solvent, but it can also be converted into a range of valuable derivatives including 1,3-propanediol (PDO), propylene glycol, epichlorohydrin, and a range of polymers for plastic, PLF and fibre applications (e.g., polyesters and polyurethanes) [47, 48, 105]. Some of these are existing products normally derived from fossil feedstocks and making them from glycerol may provide a smart route based on a waste feedstock.

Glycerol can be fermented to yield PDO. PDO is mainly used to make the polyester polytrimethylene terephthalate (PTT) for use in fibres in carpets but also has applications in polyurethanes, and home and personal care products [47]. 1,3-propanediol (PDO) can be derived from fossil propylene, but commercial bio-PDO and some of its derivatives are available [1, 47, 63].

Fossil based propylene glycol is also a derivative of propylene. Bio-based propylene glycol is produced at commercial scale from glycerol [1]. Propylene glycol is used in products such as hydraulic and brake fluids, anti-freeze, pharmaceuticals, and personal care products, but also in the production of polyesters [1]

Epichlorohydrin is mostly produced from fossil-based propylene, but production from glycerol takes fewer steps and avoids some of the harsh conditions required for production from propylene [65]. Bio-glycerol derived epichlorohydrin was estimated to make up 15% of the market in 2017 [47]. Epichlorohydrin is used in the production of epoxy resins, which are used in paints and coatings, composite materials, and adhesives [47].

4.3 Levoglucosan and levoglucosenone

Levoglucosan is usually formed by pyrolysis of lignocellulosic biomass, a process which results in a mixture of levoglucosan alongside other potentially valuable compounds [113]. The levoglucosan can then be converted directly into various high added-value platform chemicals including 5-hydroxymethylfurfural, levoglucosenone, and styrene, or into glucose [113]. Levoglucosan is considered an interesting, novel bio-based platform chemical but it is not yet produced at scale.

Levoglucosenone is a derivative of levoglucosan but it can also be produced directly by pyrolysis of lignocellulosic biomass [114]. Levoglucosenone is an example of what is known as a chiral molecule, meaning it has a feature in its chemical structure that makes it useful in the production of fine chemicals and pharmaceutical [114]. It can also be converted into a range of valuable chemicals for use in polymers, for example caprolactam (which is usually produced from fossil-BTX aromatics), and molecules such as 5-HMF (see below) [47]. There is particular interest in conversion of levoglucosenone into cyrene, a novel bio-based solvent that can potentially replace hazardous petrochemical solvents in a number of applications [36, 115]. Pilot scale production of levoglucosenone and cyrene has been achieved using forestry waste, and a commercial plant is under construction [115].

4.4 5-hydroxymethylfurfural (HMF)

HMF has been identified as a potentially important bio-based platform chemical because it can be converted into a range of useful derivatives [116-118]. HMF is produced by catalytic conversion of sugars [116, 117]. Full scale commercial production is yet to be achieved, and the cost is expected to be high compared to fossil alternatives because of expensive feedstocks and energy intense processes [118-120]. Small scale production via thermocatalytic conversion of lignocellulosic biomass has been achieved, but for many processes there are ongoing challenges associated with yield and economics [118].

Research has demonstrated the conversion of HMF into several potentially valuable derivatives with numerous applications. This includes drop-in replacements for a number of chemicals currently produced from fossil feedstocks, such as DMF, a solvent, caprolactam, a monomer used for nylon-6 production, and a number of intermediates used for plastic, pharmaceutical, and agrichemical production [47, 117]. There are also derivatives which are themselves novel bio-based platform chemicals, such as 2,5-Furandicarboxylic acid (FDCA) and levullinic acid, and researchers have developed HMF derived surfactants [1, 47, 105, 116, 117, 121]. HMF also has potential in the production of alternatives to formaldehyde resins, which are commonly used as adhesives in products like plasterboard but are faced with increasing concern over the potential for hazardous emissions from products. Research has demonstrated that HMF can be used to replace formaldehyde in common resins or can be the basis for new adhesives for a range of purposes [85, 122].

A number of different technologies for FDCA production from HMF have been developed [123]. FDCA production is in the pipeline with the first commercial plant, which will produce FDCA from wheat derived sugars via HMF, under construction in Netherlands [1, 124]. The main driver for interest in FDCA appears to be the production of PEF (polyethylene furanoate), a bio-based alternative to PET where the FDCA is replacing petrochemical terephthalic acid [1, 116]. FDCA also has the potential to be used in a variety of other novel plastics, including nylons and biodegradable plastics, and can be an intermediate for production of some pharmaceuticals, agrochemicals, and fuels [1, 47, 116, 119].

Only small-scale production of levullinic acid from HMF has been achieved so far but more appears to be in the pipeline [47, 125]. Levullinic acid has several potentially interesting derivatives including 2-methyl-THF (a novel bio-based solvent), polymers, plasticizers and fine chemicals that can be used in the production of agrichemicals [36, 105, 126].

5. Polymers

Polymers are large molecules made from many smaller chemical building blocks (known as monomers) joined together in chains which are joined together in polymerisation reactions. Polymers can be categorised by the types of monomers used and the chemical bonds that join them together. For example, categories of polymer discussed in this report are:

- Polyolefins are made by polymerisation of olefins. Examples include polyethylene (made by polymerisation of ethylene) and polypropylene (made by polymerisation of propylene).

- Vinyl polymers are made by polymerisation of vinyl monomer, for example polyvinyl chloride which is made by polymerisation of vinyl chloride.
- Polyesters contain monomers joined by a certain type of chemical bond known as an ester bond and they are typically made through polymerisation of two types of molecules: polyols and carboxylic acids. Examples include Polyethylene Terephthalate (PET, formed by a reaction between terephthalic acid (or dimethyl terephthalate) and mono ethylene glycol) which is often simply referred to as polyester, and polylactic acid (PLA, formed by polymerisation of lactic acid).
- Polyurethanes contain monomers joined by a certain type of chemical bond known as a urethane bond and they are typically made through polymerisation of two types of molecules: isocyanates and polyols.
- Polyacrylics or polyacrylates are made by polymerisation of acrylate monomers, which are derivatives of acrylic and methacrylic acid. Examples include polymethylmethacrylate (PMMA) which is a polymer of methyl methacrylate (MMA) and is referred to as acrylic.

These common structures within these group means there are some commonalities in the properties within a group, but the chemical and physical properties are also influenced by other factors such as the specific monomers used, the length and branching of the polymer chain, and what additives may be present. The variation in properties also means there is a huge variety of applications. Plastics are the most well-known use of polymers but they are also used in other forms, such as rubbers, synthetic fibres, and liquid formulations.

5.1 Plastics

Plastics are materials formed from polymers with properties varying from rigid to flexible. Global plastics production was approximately 391 Mt in 2021 and plastic is the largest output of the global chemical sector [87, 127, 128]. Since large scale production of plastics began in 1950s they have increasingly replaced traditional materials like glass because of their versatility and desirable properties, such as their low cost, durability, light weight and resistance to degradation [129, 130]. Plastic is used in packaging (44% demand in 2021), buildings and construction (18%), automotives (8%), household items and electrics (7% each) and a variety of other applications [127]. Plastics are ubiquitous in modern society because of their useful properties, but they contribute to two of the greatest challenges we face globally: pollution and climate change [130, 131].

Additives such as dyes and plasticisers are often used in plastic production to achieve the desired material properties. Many additives that are used are toxic, and some are carcinogenic, endocrine disrupting (i.e., interfere with the bodies hormonal systems), or are persistent or bio-accumulative (i.e., do not degrade and so accumulate in living organisms) [132]. These additives can pose a risk to people and the environment, and recycling can lead to further distribution of additives if not properly managed [132]. Though additives are a clear part of the plastic sustainability challenge, the following discussion is focused on the polymers used to make plastics rather than the additives. Some novel bio-based plasticizers (a kind of additive used in plastics), are discussed in section 8.1.

At end of life, plastic waste generally goes down one of four routes: recycling, incineration, leakage/release into environment, or landfill. Plastic pollution occurs due to plastics entering the environment either because of leakage along the supply chain, incorrect disposal at end of life, or loss of plastic pieces or microplastic particles during use. Many common plastics can be recycled but recycling rates remain low in many regions of the world, often due to challenges associated with collection or processing (e.g., contamination of plastic waste, presence of additives, or product design that makes recycling difficult) [127, 130, 133].

The plastics industry is dominated by a small number of material types. Drop-in bio-based plastics are made by substituting fossil-based monomers in polymer production with bio-based or bio-attributed equivalents. At lab scale almost any monomer required for plastic production can be made from biomass and so drop-in bio-based versions of many major plastics have been developed, though many are not yet commercially available [133]. Bio-attributed forms of many commonly used plastics are commercially available.

There are also a variety of novel bio-based plastics some of which have new or improved properties. For example, biomass lends itself to the production of bio-degradable plastics[2], which are gaining attention as a tool to help tackle plastic pollution [65]. Many biodegradable plastics require industrial facilities for rapid biodegradation and improper handling of these materials at end of life can mean they end up in conditions under which they do not biodegrade or degrade slowly [133-135]. There is also some concern around methane emissions from biodegradable plastics in landfills and contamination of recycling streams which can cause challenges for existing recycling systems [136, 137]. So, biodegradable plastics are not a silver bullet to address plastic pollution, but they are particularly useful for applications where recycling is challenging. This includes applications that result in contamination with organic material or lead to plastic entering composting facilities (e.g., food packaging that is hard to clean such as coffee pods or bags for food waste) or applications where it is hard to fully recover the plastic from the environment after use (e.g., tree shelters, agricultural mulching films, or fishing gear) [17, 65, 67, 205, 209-212]. Biodegradable plastics often have poor mechanical properties compared to conventional plastics (e.g., more brittle) and this can impact their use in certain applications, but using them in blends with other polymers or in composite materials (see section 5.5) can help to overcome this [133, 135]. For more detailed discussion of bio-degradable plastics the topic the following resources might be of interest: [133, 134, 138, 139].

Currently, bio-based plastics make up a small proportion of global plastics demand, with the most common application of bio-based plastics being in plastic packaging [35, 127, 128]. Many drop-in and novel bio-based plastics have been developed, but not many are being produced commercially and even those are often in small volumes [133].

5.1.1 Polyethylene

Polyethylene is the highest demand plastic globally. Demand in 2021 was 105 Mt accounting for roughly 27% plastic demand [127]. Polyethylene is produced by polymerization of the primary chemical ethylene [1, 7]. Polyethylene comes in different forms: Low density (LDPE) and linear low density (LLDPE) (14.4% of the market), and high density (HDPE) and mid density (MDPE) (12.5%) [127]. It is very versatile, with the different forms (LDPE, LLDPE, HDPE, and MDPE) having different properties.

The main use for polyethylene is in packaging (e.g., food packaging, bottles, films) and this accounts for over 50% of polyethylene demand. Some polyethylene is also used in construction (e.g., flooring, countertops) and a variety of other applications such as consumer goods (e.g., grocery bags, toys, buckets) [127, 140]. This means that most polyethylene is used in short lifetime products. Polyethylene is recyclable and non-biodegradable but end of life fate depends on the product design and use and waste management practices.

Bio-polyethylene is obtained by polymerisation of bio-ethylene (see section 3.1). Bio-attributed and bio-based polyethylene are commercially available [30, 31].

5.1.2 Polypropylene

Polypropylene demand was 75 Mt in 2021 accounting for 19.3% global plastic [127]. The production of polypropylene takes place by polymerisation of the primary chemical propylene. The main use for polypropylene is in packaging (e.g., food packaging, pallets). Other major uses include construction (e.g., pipes, insultation films), automotive (e.g., bumpers, internal panels),

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[2] It is important to note that biodegradable is not synonymous with bio-based: not all bio-based plastics are bio-degradable and not all bio-degradable plastics are bio-based.

and consumer goods (e.g., toys, sanitary products, buckets) [127, 141, 142]. This means the main use of polypropylene is in short lifetime products, but it also has a range of uses in medium and long lifetime products. Polypropylene is recyclable and non-biodegradable, but end of life fate depends on the product design and use and waste management practices and current recycling rates are low.

Bio-polypropylene is obtained by polymerisation of bio-propylene (see section 3.2). Bio-attributed polypropylene produced from bio-attributed propylene is commercially available [42-44, 143].

5.1.3 Polyvinyl chloride (PVC)

PVC is produced by polymerization of vinyl chloride monomer which is a derivative of the primary chemical ethylene (see section 3.1) [1]. PVC demand was 50 Mt in 2021 accounting for 13% global plastic [127]. Most PVC is used in construction (e.g., pipes, window frames, flooring, roofing) in long lifetime applications [127, 144].

Bio-PVC is obtained by polymerisation of bio-vinyl chloride, which is derived from bio-ethylene. Bio-attributed PVC derived from bio-attributed ethylene is commercially available [39, 145]. However, PVC poses some additional sustainability and safety challenges on top of those that are common to all plastics and so it may be that alternatives to PVC instead of drop-in replacements are required in the future [146]. PVC is a major source of harmful chemical residues indoors because of the kind of additives (plasticisers) it often contains [147]. There can be a risk to people and the environment from manufacturing and end-of-life disposal of PVC because of the hazardous materials and toxic emissions [146]. PVC can be recycled but recycling rates are low, and additives in PVC raise additional questions around waste management [146].

5.1.4 Polyethylene terephthalate (PET)

PET is a polyester produced by the polymerization of two monomers: ethylene glycol (derived from ethylene (see section 3.1)) and terephthalic acid (derived from xylene (see section 3.4)) [45]. PET demand was 24 Mt in 2021 accounting for 6% global plastic [127]. The majority of PET is used in packaging, particularly in the food and drinks industry and for bottles [22, 45, 127]. This means the major uses of PET is in short lifetime products. PET is non-biodegradable and recyclable. PET recycling, particularly PET bottles, is relatively high compared to other plastic products [148]. It is also used in textiles which is discussed in section 5.4.

Of the two monomers required for PET production, only ethylene glycol is currently commercially available in bio-based form. Partly bio-based PET, made from bio-ethylene glycol and fossil PTA (resulting in a product that is about 30% bio-based), is commercially available [133, 149]. Bio-based production using bio-based PTA as well as bio-based ethylene glycol has been demonstrated [34, 93].

5.1.5 Polystyrene (PS)

Polystyrene is produced via polymerisation of styrene, a monomer derived from ethylene and benzene (see sections 3.1 and 3.4). Polystyrene demand was 21 Mt in 2021 accounting for 5% global plastic [127]. Polystyrene comes in both solid and expanded forms, which deliver different properties.

The main uses of polystyrene are in packaging and construction (e.g. insulation or stabilisation materials), but it is also used in a variety of other applications such as electronics and automotives [127, 150]. This means it is used in applications ranging from short to long lifetimes. Polystyrene is non-biodegradable and recyclable, but currently it is not commonly recycled.

Bio-attributed polystyrene produced via polymerisation of bio-attributed styrene is commercially available [41, 151]. Bio-based styrene is not yet available and so neither is bio-based polystyrene. Research has also produced novel styrene alternatives from biomass that be used to make alternative polystyrene like materials [152].

5.1.6 Polyurethanes

Polyurethanes demand was 22 Mt in 2021 accounting for 5.5% global plastic [127]. In contrast to the plastics above, which are based on specific polymers, polyurethanes are a group of plastics based on various polyurethane polymers. Polyurethanes contain monomers joined by a certain type of chemical bond known as a urethane bond and they are typically made through polymerisation of two types of molecule: isocyanates and polyols [153]. There are many isocyanates that can be used in polyurethane production, however, the most used are toluene diisocyanate (TDI), which is derived from toluene (see section 3.4), and methylene diphenyl diisocyanate (MDI), produced from aniline and formaldehyde (derivatives of benzene and methanol, see section 3.3) [153]. Many different polyols are used in polyurethane production, but the most common examples are derived from ethylene oxide or propylene oxide [153, 154].

The properties of polyurethanes can be tailored by changes to the monomers used, the polymer structure, the polymerisation conditions, and any additives used. As a result, they can have widely varying properties, making them very versatile. Polyurethane plastics have many different applications including construction, automotive, electrical goods and a number of others [127, 153]. They are often used in foams: rigid polyurethane foams are insulating materials with common uses in construction, industrial applications, transport, and household appliances (e.g., refrigerator); flexible polyurethane foams are used in household items (e.g., furniture, cushions) and automobiles (e.g., car seats) [153, 155, 156]. The wide variety of applications mean there are widely varied lifetimes for polyurethane goods, though many applications appear to be in medium and long lifetime products. Polyurethanes are non-biodegradable. They are recyclable but recycling rates are low, and they are usually landfilled [154]. Polyurethane can also be used as elastomers and liquid formulations and these applications are discussed in sections 5.2 and 5.3 [153].

Polyols for polyurethane production can be sourced from biobased materials. The most common examples are polyols derived from plant oils (e.g., derived from fatty acids), but researchers have also developed polyols from other biomass platforms such as lignin and from bio-based platform chemicals such as succinic acid [153, 157, 158]. Often these have unique properties and to create a polyurethane with properties more similar to a fossil-based version more extensive modification of the bio-based polyols is required [153]. A range of novel polyurethanes based on bio-based polyols and fossil-based isocyanates have been developed by researchers and some are now commercially available [109, 153, 157, 159, 160]. Bio-based versions of the common isocyanates used for polyurethanes are not yet available. Safety concerns around these isocyanate monomers have led some researchers to look into novel bio-based alternatives [133]. Bio-attributed forms of some common polyurethane monomers are now available, and so are some examples of bio-attributed polyurethanes [98, 161, 162].

5.1.7 Other plastics

There are also many other fossil-based plastics produced in smaller volumes than those discussed above [127]. For example, polyacrylics or polyamides (i.e., nylon), which are commonly used in applications such as textiles and so are discussed in more detail below. Polyacrylics (or polyacrylates) are made by polymerisation of acrylate monomers, which are derivatives of acrylic and methacrylic acid. The most common example is polymethylmethacrylate (PMMA) which is a polymer of methyl methacrylate (MMA) and is referred to as acrylic. PMMA has numerous applications including in construction, automotives, electronics, and other household items [72]. Bio-based PMMA is not yet available, but efforts to develop smart routes to MMA and therefore PMMA are underway. A range of bio-attributed acrylics are available [163].

5.1.8 Polylactic acid (PLA)

PLA is a bio-based polyester formed via polymerisation of lactic acid, which is produced via fermentation [1, 133, 164-166]. Several companies worldwide are currently producing PLA, with most production in the USA, Thailand, and China [165, 166]. Global production capacity is estimated at over 250 kT [133].

PLA is a biodegradable plastic: it can be composted in industrial composters but takes more than 1.5 years to degrade in the ocean [133]. It can also be recycled, though where there are not appropriate compositing or recycling facilities in place it is still sent to landfill or incinerated.

The properties of PLA vary depending on how it is made, and affect which applications it can replace fossil-based plastics in. Currently, PLA is mainly used in packaging (e.g., as replacement for polyolefins [133]), though there are applications in textiles, consumer goods, agricultural materials, and parts in the automotive industry [167]. PLA is a fairly brittle material, something which is common amongst bio-degradable plastics, and this has limited its use in higher stress applications.

5.1.9 Polyhydroxyalkanoates (PHAs)

PHAs are polyesters produced directly by fermentation process [164]. This means that PHAs are produced in microorganisms, rather than being manufactured from bio-based building blocks by the chemical industry as is the case for other polymers like PLA or bio-PE [47, 135, 168]. There are different kinds of PHA with varying structures and properties [135, 168]. There is some commercial production but fairly limited so far, and the global production capacity of PHA is estimated at over 30 kT [47, 133, 135, 168].

The main use for PHAs is expected to be in packaging, biomedical applications (such as implanted medical devices and drug delivery systems), and agricultural uses (such as films) [164]. PHAs can be composted in industrial facilities but some PHAs are biodegradable in soil and marine environments [133, 135, 164, 168]. Degradation rate in different environments depend on the nature of the PHA used [135, 164]. As with PLA, there could be issues if PHA contaminated existing recycling streams.

5.1.10 Polyethylene furanoate (PEF)

PEF is polyester like PET but the PTA used in PET is replaced by FDCA (see section 4.4) [1, 116, 133]. FDCA is polymerised with bio-ethylene glycol to form the bio-based polymer PEF. Commercial production of has not yet been realised, but production of FDCA and PEF is expected to begin in 2024 [124].

PEF has similar properties to PET in many regards and may even have improved properties for some applications [133]. As a result, it could directly replace PET plastic in a number of applications [133].

5.1.11 Natural polymer derived plastics

As well as producing bio-based polymers and plastics synthetically from bio-based building blocks, there are a variety of natural polymers (e.g., starch, alginate, cellulose) which can be used to make plastics [133]. The focus of this report is synthetic materials and chemicals produced from biomass so plastics from natural polymers are not discussed in detail here.

5.2 Polymers in liquid formulations

Polymers in liquid formulations (PLFs) are polymers dissolved in a solvent or carrier, often in mixtures with other chemical components. Though not as well-known as other polymer applications like plastics and textiles, they play an essential role in many products such as personal care and cleaning products, paints, and adhesives, and many industrial applications and water treatment processes [52, 169, 170].

PLFs are used in formulations that remain liquid on application (e.g., home and personal care products, agrochemicals, water treatments, or lubricants) or curable formulations that form solids upon application (e.g., adhesives, sealants, paints, coatings, and inks). PLFs in curable formulations tend to be in much higher concentrations than PLFs in formulations that are designed to remain liquids [52, 169]. The PLFs sector is small compared to the plastic sector, with a total demand of approximately 36 Mt a year, but they are often used in higher value applications [52]. Many applications of PLF only use small quantities of polymer, though curable formulations tend to use higher concentrations than formulations that are designed to remain liquid [52, 169]. The largest (by volume) application of PLFs is paints and coatings, followed by adhesives and sealants [169].

PLFs come with their own sustainability challenges, these have received less attention than sustainability issues associated with other polymer applications until they were recently highlighted in a series of reports published by the Royal Society of Chemistry [52, 169, 170]. PLFs contribute to GHG emissions, most are derived from fossil feedstocks, and their use can result in them entering the environment where they tend to break down very slowly [52, 170]. Applications that remain liquid result in polymers being dispersed into wastewater treatments systems and/ or the environment. [52, 170]. Curable PLFs tend to be incinerated or landfilled at end of life, often because separating them from substrate materials (e.g., paint on the surface of wood, or adhesive in woodchip board) can be challenging and this is a barrier to recycling [52]. Alongside new approaches to PLF waste management and circular economy, there is a need for new polymers that are non-toxic and biodegradable and have improved material efficiency and reduced lifecycle GHG emissions, and here bio-based PLFs may play a role [52, 170]. Bio-based PLFs make up a small share of the market to date, but there seems to be growing interest from several sectors [52, 170-172].

Many different polymers are used as PLFs, with some of the most common types being: polyacrylics, polyesters, polyurethanes, vinyl polymers, and a variety of water-soluble polymers [52, 170]. These are mostly derived from fossil feedstocks via the primary chemicals described in section 3. To date there are relatively few examples of PLFs that have commercially available drop-in bio-based alternatives. Research has demonstrated many novel bio-based polymers for PLFs, often focusing on beneficial new functionalities such as biodegradability, and some of these have reached commercial deployment [52, 170, 172-177].

Polyacrylics are formed from acrylate monomers. Bio-attributed and partially bio-based polyacrylics are available as drop-in replacements for polyacrylics in some PLF applications [163, 178]. There are also examples of novel bio-based polyacrylics, such as one which is commercially available for use in cleaning products [177].

Polyesters are typically made through polymerisation of polyols and carboxylic acids, many of which are relatively easy to produce from bio-based feedstocks [172]. PET, a common plastic discussed in section 5.1.4, is an example of a polyester. Drop-in polyesters have been developed by researchers and some are available commercially [179]. A range of novel bio-based polyesters are also available which includes PLAs and PHAs,discussed in the context of plastics [172].

Common vinyl polymers used in PLFs include polyvinyl alcohol and polyvinyl acetate, which rely on a monomer derived from ethylene and acetic acid, both of which are available in bio-based and bio-attributed form [52, 77, 170]. Novel vinyl polymers, including biodegradable vinyl polymers, are also being developed [170].

Polyethylene glycol PEG, formed by polymerisation of ethylene oxide, is another common PLF in home and personal care products [170]. Bio-based PEG, from bio-ethanol derived bio-ethylene oxide, is commercially available [37].

Polyurethanes were discussed in the context of plastics in section 5.1.10. Novel bio-based polyurethanes have also been developed for PLF applications in agriculture, paints, coatings, and adhesives, with some potentially being able to replace problematic formaldehyde resins in applications such as plywood [52, 153].

Some natural polymers, such as starch or modified lignin, also have potential as PLFs [170, 180]. There are also examples of proteins with natural adhesive properties being developed for commercial use [172].

5.3 Rubbers

Like plastics, rubbers are polymer-based materials. Rubbers differ from plastics in their material properties in that they are elastic, and this is down to the type of additives used as well as the nature of the polymers [181]. Rubbers include both natural rubber, which comes from the tree *Hevea brasiliensis,* and synthetic rubbers which are mostly derived from fossil feedstocks [181]. In 2022 roughly 15 Mt of natural rubber and 15 Mt synthetic rubber was produced [182]. Natural rubber has many desirable properties, but for some applications synthetic rubbers are better suited, and the properties of synthetic rubber can also be varied.

Synthetic rubbers are used in a range of applications, with the main one being in the production of tyres and other automotive applications, industrial and consumer goods, and footwear, and construction [183, 184]. Synthetic rubbers are hard to recycle, but they are increasingly being broken down into crumbs and used in applications like road surfacing and flooring.

The main types of synthetic rubber are styrene butadiene rubber (SBR) and polybutadiene rubber (BR) [181, 184]. Styrene butadiene rubber is based on a polymer of styrene, a derivative of ethylene and benzene (see sections 3.1 and 3.4), and butadiene, which is produced alongside other primary chemicals like ethylene during naphtha processing. Neither monomer is yet available in bio-based forms, though smart routes via direct fermentation have been developed at lab scale and production of butadiene from bio-ethanol has been demonstrated at pilot scale [185-187]. Styrene, butadiene, SBR, and BR are available in bio-attributed forms [41, 188].

There are many other synthetic rubbers including PVC and Polyurethane rubbers which rely on the polymers described for PVC and polyurethane plastics [181, 184]. Another common synthetic rubber is ethylene propylene diene monomer rubber (EPDM) [181, 184]. EPDM is made from ethylene and propylene, along with an additional monomer which can vary. Partially bio-based EPDM made using bio-ethylene is available [189].

Several novel bio-based synthetic rubbers have been developed by researchers, and as with other polymer applications there is an interest in developing novel rubbers with properties such as biodegradability [181, 190].

5.4 Synthetic fibres

Global fibre production reached 111 Mt in 2019 [191]. Synthetic fibres derived from fossil feedstocks accounted for almost 70% of this. Natural fibres such as cotton (over 20% demand), wool and manmade cellulosic fibres[3] are also a significant market [191].

Synthetic fibres have properties such as strength, durability, shape retention, and are quick drying, which make them more desirable than natural fibres for many applications. Synthetic fibres are mainly used in clothing and home furnishings [193]. Some polymers used for synthetic fibres can be recycled, but the reality is that fibre and textile recycling rates are very low even for these polymers. Recycling is made more complex for mixed fibres (e.g., polycotton, a mixed fibre of polyester and cotton), which are commonly created to achieve certain properties or reduce costs, and when additives such as dyes are present[4] [195-197]. Textiles made from synthetic fibres also shed during use and laundering, releasing plastic microfibres that remain in the environment because most of the polymers used are not biodegradable [197]. The textile

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[3] Man made cellulosic fibres are based on modified cellulose. The most common is example is viscose, which is produced by chemical modification of wood cellulose in a highlight polluting process [191,192].

[4] There are various new technologies being developed to improve textile recycling, including routes based on biotechnology [194-196].

industry is also a source of significant GHG emissions, large volumes of waste, and pollution from chemicals like dyes used in production processes [197]. The textile industry is coming under pressure to address these environmental impacts. As part of the efforts to create more sustainable textiles[5], several textile companies have committed to renewably sourced textiles, from recycled or bio-based sources [191].

Bio-based fibres are available, but do not yet make up a significant proportion of the market. They offer opportunities to reduce the GHG emissions associated with synthetic fibres, though like other bio-based products such reductions are not universal and it is important to consider wider sustainability impacts to avoid burden shifting [198]. A range of novel bio-based fibres have been developed, often using bio-based monomers that are more readily available than those required for drop-in products, and some offer beneficial properties such as biodegradability.

The most common synthetic fibre is polyester (fibres of polyethylene terephthalate, PET) which accounts for approximately 52% of global fibre production [191]. As described in section 5.1.4, polyester is made from the monomers MEG and PTA, and though bio-MEG is commercially available, bio-PTA is still under development [1, 49, 50, 93]. Partially bio-based polyester fibre made using bio-MEG and fossil-PTA is commercially available [199, 200]. A range of novel polyesters based on polymers other than PET have also been developed. One example is polytrimethylene terephthalate (PTT), a polymer of PTA with a different monomer in place of MEG, namely propanediol. PTT can be made from fossil feedstocks but production of fossil propanediol tends to be costly, so it isn’t widely used [198]. Bio-propanediol produced by a smart, direct route seems to overcome this challenge and partially bio-based PTT made from bio-propanediol and fossil-PTA is commercially available [198, 201]. The novel bio-based polyester PEF (see section 5.1.10) could directly replace PET fibres in some textile applications [133]. There are also commercially available bio-based and bio-degradable polyester based fibres, including PLA [198, 200, 202-204]. PLA was discussed in the context of plastics in section 5.1.8. It is in fact a type of polyester and it can also be used to make fibres for textiles applications. Despite the example given here, it is estimated that less than 1% of the global polyester fibre market is bio-based [191].

Another important class of synthetic fibres is polyamides. The most used polyamide fibres are nylon 6,6 and nylon 6. Nylon 6,6 is derived from hexamethylenediamine and adipic acid [205]. Bio-attributed Nylon 6,6 is available [206]. As outlined in section 3.2 smart routes to bio-adipic acid are under development, driven by the particularly high emissions associated with the production of adipic acid from primary chemicals [1, 100, 102]. Similarly, smart routes to bio-hexamethylenediamine have been investigated. Fermentation derived, bio-adipic acid and bio-hexamethylenediamine are reportedly being scaled up, meaning bio-based nylon6,6 may be commercially available soon [207, 208]. Nylon 6 is derived from caprolactam, which is a derivative of BTX aromatics [205]. Smart routes to bio-caprolactam and hence bio-nylon 6, are under development [1, 209, 210]. A range of novel bio-based polyamides/ nylons based on novel bio-based monomers have also been developed. Those that are commercially available tend to be derived from monomers derived from fatty acids in castor oil [191, 205, 211, 212]. Novel bio-based polyamides/ nylons based on other feedstocks have been shown at lab scale [205].

Natural fibres are not within the scope of this report, which is focused on products of the chemical industry, but it is worth noting that underutilised natural fibres derived from plants like hemp are gaining interest from some in the fibre industry.

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[5] Alongside approaches to change feedstocks and materials in fibres, it must be noted that textiles, particularly used in clothing, is an area where consumer behaviour and the way the industry functions will have to change as the current system of “fast fashion” and high demand is unsustainable [194, 197] .

5.5 Polymer composites

Composites materials are formed by combining at least two different materials together, and they have properties that are superior to those of the combined materials [213]. Generally, composite materials are formed by embedding fillers (fibres or nanoparticles, e.g., natural fibres, synthetic polymer fibres, inorganic particles, carbon nanotubes or carbon fibre), in a matrix material (e.g., polymer/plastic, ceramic, or metallic) [213, 214]. Here, we are focusing on composites with a polymer matrix. Polymer matrix composites can be formed using a whole range of organic polymers [213]. For example, polyesters, polyamides, and polyurethanes are often used as the matrix materials [214].

Polymer composite properties vary according to the components used, but they tend to have low densities and high strengths compared to alternative materials like metals and they can have other beneficial properties such as wear resistance [214]. As a result, they are increasingly used in the production of automotives and other vehicles, wind energy (structural components of wind turbines) and other energy applications, aerospace, defence, and construction [214, 215]. Recyclability varies according to the polymer composite in question. Some are already being recycled, but for others approaches to recycling have yet to be developed or implemented and materials are incinerated or landfilled at end of life [216, 217]. The low recycling levels coupled with the fact that polymer composites are fossil-based means that innovation is needed to make composites more sustainable [215].

Bio-based plastics can be used as the matrix components of polymer composites [215, 218]. This could be through drop-in replacements for the common fossil derived polymers that are used in polymer composites (e.g., bio-based polyester or bio-based polyamide) but there are also opportunities to utilise novel bio-based plastics in composites [214, 216]. PLA composites, for example, have improved mechanical properties compared to PLA alone, making it more suitable for use in applications such as aerospace and automobile manufacturing [214, 219].

There are also opportunities for using bio-based fillers for composites [215, 218]. Natural fibres are already used in some polymer composites, but biomass could also be used as a feedstock to produce some of the other common fibres and particles. For example, carbon fibre produced from bio-based polyacrylonitrile is being scaled up for use in composites manufacturing and direct routes to carbon fibre from lignin are also being developed [220]. Researchers have also created polymer composites with using fillers made of biochar, the solid product of biomass pyrolysis that is formed alongside pyrolysis oil [221].

6. Solvents

Solvents are fluids that are used to dissolve other substances [222]. Organic solvents have many important applications in industry and in consumer products. They are used in industry for extraction, separation, and purification, and to dissolve reagents for chemical reactions [48], and are an essential ingredient in many cleaning products, perfumes, varnishes, and paints [48, 222, 223]. The global solvent market was 28 Mt in 2022 and with paints and coatings being the primary application [223, 224]. Different types of solvents include oxygenated solvents (e.g., alcohols such as isobutanol or ethanol, or acetone), hydrocarbon solvents (e.g., cyclohexane or aromatics such as toluene), and halogenated solvents (e.g., solvents containing elements like chlorine, such as dichloromethane (DCM). Most organic solvents are derived from fossil feedstocks via the primary chemicals discussed in section 3, and in fact a number of key platform chemicals are also important solvents (e.g., ethanol, toluene, and acetone) [222].

Many solvents are incinerated after use [222] but there is also leakage into the environment through accidental release, waste management processes, or evaporation and sometimes solvents used in manufacturing sometimes remain in end products in small amounts. Solvents can contribute significantly to waste generation and GHG impacts in industrial processes and products [36, 222]. Many commonly used organic solvents are also toxic and flammable or explosive, and they are often volatile organic compounds (VOCs) which impact air quality [222]. As a result, solvents can pose risks to human health (e.g., of workers in industry or consumers) and the environment even if used in small quantities [36, 48, 81, 222]. Green chemistry approaches encourage the substitution of certain high-risk solvents for alternatives that pose less risk to human health or the environment, and in many regions of the world this is increasingly supported by regulations which restrict the use of some solvents in applications where they pose a particular risk [36].

Drop-in replacements for several important organic solvents are available and many compounds that are of interest as biofuels or platform chemicals also have applications as solvents or have derivatives that are important organic solvents [81]. Commercially available drop-in solvents include bio-ethanol, bio-acetone, and bio-butanol, mainly produced via fermentation [1, 48] (beginning UK production soon [66]), and bio-ethyl acetate which is produced from bioethanol [36, 48, 81, 225, 226] bio-ethyl acetate accounted for 22% ethyl acetate produced in the EU in 2019 [35]). Ethanol, acetone, butanol, and ethyl acetate (fossil or bio-based) are all oxygenated solvents that can be used as safer and less toxic replacements for other more problematic solvents, for example ethyl acetate can be used as a less hazardous replacements for solvents such as dichloromethane (DCM, a volatile compound and potential neurotoxin). There seems to have been less activity focused on producing drop-in replacements for hydrocarbon solvents (which will often be more difficult to produce from biomass) and solvents that are particularly hazardous or toxic.

In fact, a lot of activity in the bio-based solvents space seems to be focused on novel solvents, particularly where they can displace hazardous solvents or have performance benefits [36]. Some of the novel bio-based platform chemicals and biofuels have applications as solvents [36, 81] for example, glycerol (see section 4.2) has applications as a solvent as do some of its derivatives [81]. Other promising bio-based solvents include Cyrene, 2-Methyl-THF, and ethyl lactate all of which can potentially replace hazardous solvents (e.g., dimethylformamide (DMF) a liver toxin) in some applications. Cyrene is a derivative of levoglucosenone (see section 4.3) that was developed at the University of York [36, 115]. 2-Methyl-THF is produced from levullinic acid or furfural [36]. Ethyl lactate is derived from lactic acid (see section 5.1.8). It is non-toxic and biodegradable and is already used in products such as paints and coatings, gums, food additives, and cosmetics, and industrial applications including cleaning [1, 48, 227].

Bio-based solvents can have sustainability benefits, potentially enabling reduced lifecycle GHG emissions and in some cases acting as a safer alternative to toxic and hazardous solvents [36, 81]. Some novel solvents also have new functionalities that improve performance in certain applications. However, in some cases novel bio-based solvents have undesirable properties, for example, many are more viscous or less stable than conventional solvents they might be intended to replace [81]. Having a solvent with the right chemical and physical properties is essential to a process or product working successfully and so the properties of a bio-based solvent will remain a deciding factor in whether it is taken up or not. To be viable bio-based solvents must also be cost competitive with the existing solvents they might displace, and this is often a challenge [36, 48]. Bio-based butan-1-ol accounted for roughly 2/3 of the market until the 1950s but falling fossil feedstock prices lead to the bio-based product becoming economically competitive [48]. Currently the market share for bio-based solvents is still small, an estimated 1.5 % of the EU solvent market in 2019 was bio-based [35] but there is a growing market for sustainable solvents in various industries [224]

7. Bitumen

Bitumen is an adhesive substance that is a mixture of high molecular weight hydrocarbons obtained from heavy oil fractions (i.e., it is a by-product of oil refining, rather than being derived from chemical industry feedstocks) [128, 228]. It is produced in large volumes, with over 100 Mt being produced globally a year, and over 700 kT annually in the UK [128, 229, 230]. Bitumen is often used in the form of asphalt, where bitumen acts as a binder to hold together aggregates such as sand or waste plastic. The main application of bitumen is in road and pavement surfacing, but it also has other applications in construction, such as roofing and waterproofing [231], most of which are likely to have long lifetime. Bitumen can be reused and recycled if appropriate facilities are in place.

Rather than trying to recreate the extract hydrocarbon mixtures that are seen in fossil derived bitumen, a range of novel bio-binders for replacing bitumen have been developed. Often these are based on biocrudes or bio-oils from thermochemical processing of biomass feedstocks, especially wastes [232]. Another promising option for bio-based bitumen in the use of lignin as a binder [233]. These bio-binders tend to be mixed with fossil bitumen rather than replacing it totally, with bio-binders sometimes replacing less than 10% fossil bitumen [232, 233]. There is hope that with further research it may be possible to create bio-binders that could displace more of the fossil bitumen in the mixture or even do away with it completely [232-234]. Bio-bitumen is an area of growing interest due to the potentially sustainability benefits, and although most of the work thus far has been at lab scale, there are also some examples of bio-bitumen in road trails and a bitumen using a portion of bio-based binder is now being used to produce asphalt by a company in the UK [235, 236].

Durability and performance over longer timeframes are very important features for applications of bitumen. Bio-bitumens do not have the same chemical composition as traditional fossil derived bitumen, and this can impact their performance. Wide scale deployment of bio-bitumen will depend on whether they can perform at the desired standards over these long timeframes. Studies thus far have shown that some examples of bitumen perform well but others have issues that lead to them aging or fracturing more rapidly than fossil bitumen [232]. There is a need for detailed and long-term studies to understand how these impacts they performance and develop better bio-bitumen, especially if in the future bio-binders can replace higher proportions of the fossil bitumen. Additionally, variations in feedstocks and processes lead to bio-bitumen with different properties which is a challenge when it comes to applications such as road surfacing, where consistent and predictable performance are particularly important [232, 233]. Economics is also a major factor in deployment of bitumen, and the cost of bio-bitumen is currently a barrier to increased deployment. This can be reduced by using waste derived feedstocks and may improve as processes are scaled up and optimised.

Several studies have demonstrated that bio-binders can reduce the GHG impact of bitumen when used to particularly replace the fossil binders [228, 233, 237, 238]. Changes in features such as durability, lifetime, or recyclability of bio-bitumen compared to fossil bitumen would impact the GHG performance. As more understanding on performance is gained, especially though long-term testing of road trials, this should be included in future studies to gain a better understanding of the carbon savings achieved.

8. Fine and speciality chemicals

Fine chemicals often have complex structures and are produced at high purity, and they are building blocks for the synthesis of ingredients for things like pharmaceuticals and agrochemicals. Speciality chemicals are chemical substances where the effect they produce is key: for example, fragrances, dyes, plasticizers, or surfactants. Fine and speciality chemicals are produced in lower volumes and come with higher values attached than many of the bulk products discussed in this briefing. They still tend to be derived from the fossil feedstocks and platform chemicals at the heart of the chemical industry but demand more manufacturing steps and intermediates along the way due to their more complex structures. Complex chemical structures mean that these types of chemicals are often well suited to production from biomass feedstocks, making use of the inherent structures in biomass. In addition, some natural products that can be extracted from plants also have direct applications as high value fine or speciality chemicals and advances in engineering biology mean it is increasingly possible to modify plant systems to produce new compounds of interest [239-243].

Two examples of speciality chemicals (plasticizers and surfactants) are explored in more detail below. More information on bio-based production of other high value, low volume, fine chemicals such as pharmaceuticals and agrichemicals can be found in an upcoming report from the High Value Biorenewables Network.

8.1 Plasticisers

Plasticizers are the most common additives used in the plastics industry. They are added to make plastics more flexible and create plastics with the desired mechanical properties [132]. Demand for plasticisers was around 11 Mt per year in 2022, with a large portion of demand being PVC plastic [244, 245]. Some plasticizers are known to be persistent, bio-accumulative, or toxic and phthalates, a commonly used type of plasticizers, are endocrine disrupting chemicals [132]. Unfortunately, sometimes they have been shown to leach out of plastic products meaning they pose a risk to human health and the environment [132, 147, 244].

Some bio-attributed alternatives to fossil-based plasticizers are available, but due to growing concern around the impacts of commonly used plasticizers, there has been a lot of research activity related to novel bio-based plasticisers with biodegradability or reduced toxicity [246-248]. The nature of the structures favoured for plasticizers lends itself to the types of complex molecules that are commonly found in biomass [249]. Bio-based plasticizers are often derived from succinic acid or components of vegetable oils, or other bio-based platform chemicals such as levullinic acid [126]. There is a lot of ongoing research in this area, but there are already some commercial examples of bio-based plasticisers from succinic acid or bio-oils [110, 250]. In 2019 a JRC report estimated that in the EU biobased (or partly biobased) plasticizers made up 9% of the total market [35].

8.2 Surfactants

Surfactants are amphiphilic molecules, which means they have a water loving region (hydrophilic) and a water repelling region (hydrophobic). They are important for applications involving cleaning and to stabilise emulsions and bubbles. The most common use for surfactants is in home and personal care products, and other applications include industrial applications (e.g., food processing, industrial cleaning, mining, water treatment), agrichemicals, pharmaceuticals (as drug delivery agents), and paints [251, 252]. Surfactants differ from many of the other groups of chemicals discussed in this report, in that bio-based surfactants already make up a significant share of the market (an estimated 50% surfactants on the EU market in 2019 contained at least one constituent derived from bio-based materials [35]). Growing interest of consumers in eco-friendly products has influenced the cleaning products market, and increased demand for natural and bio-based surfactants [253]. There is a lot of industrial activity in bio-based surfactants and a particular interest in non-toxic and bio-degradable surfactants, and those which have improved performance so less needs to be used for a product to function [121, 251]. Surfactants often end up in wastewater treatment facilities or the environment after they are used, and so some regions, including the UK have regulation that requires surfactants in certain products to be biodegradable.

Surfactants are a broad category of molecules, with a variety of different structures. A large portion of the market is made up by non-ionic surfactants, cationic surfactants, and anionic surfactants. All are formed of a functional hydrophilic head group, with hydrophobic chain (tail) attached. The hydrophobic tail in many surfactants is readily derived from fatty acids from bio-oils

[121, 251]. Due to sustainability concerns around palm oil, which is commonly used as a source of fatty acids for the industry, researchers are hoping to develop fermentation derived fatty acids to displace palm oil derivatives [254]. Some surfactants have tail groups derived from fossil feedstocks, based on olefin chains either derived from heavy oil fractions or ethylene but there is potential for creating drop-in replacements from biomass through bio-based olefins from pyrolysis oil or bio-ethylene [251, 255].

Many commercially available surfactants already have bio-derived chains based on fatty acids but creating fully bio-based surfactants, with bio-based head groups is more challenging. Common anionic surfactants include Linear alkylbenzene sulfonates (LAS), which have a head group derived from benzene, and sodium lauryl ether sulphate (SLES), which is made from bio-derived fatty alcohols derived from palm oil with a head group formed from ethylene oxide (derived from ethylene) and sulphur trioxide. Cationic surfactants usually have head groups derived from ammonia. Many non-ionic surfactants have head groups derived from ethylene oxide [121, 251, 255].

Bio-attributed versions of some common surfactants are also available [256, 257]. Ethylene oxide is an important intermediate in the production of several commonly used surfactants, and so utilising bio-ethylene oxide (see section 3.1) in conjunction with bio-based tails (e.g., based on fatty acids) allows for the production of drop-in and completely bio-based surfactants. These have been launched by several companies in recent years [37, 258]. Alongside these examples of drop-in surfactants, there has been a lot of activity around the development of novel, bio-based surfactants, for example those derived from sugar, glycerol or HMF [121, 251, 259]. Some are already used commercially, for example, alkyl polyglucosides are bio-based, biodegradable surfactants formed from sugars and fatty acids that have been commercially available for many years and are used in home and personal care products, though their widespread uptake in many applications is limited by inferior performance compared to alternatives [251, 260].

There are also microbial surfactants, which are produced directly via fermentation rather than synthetised industrially from bio-based building blocks [253, 261, 262]. They tend to be biodegradable, some have anti-microbial properties, and there are examples of microbial surfactants with improved properties meaning less is required in final products [261, 263]. Some microbial surfactants are already commercially available, for example Unilever’s rhamnolipid which is used in some home cleaning products [264]. Microbial surfactants can face challenges associated with the cost of production, but some companies have been able to innovate to overcome this. For example, University of Manchester spin-out Holiferm who have recently opened their first commercial demonstration plant [265, 266].

9. Acknowledgements

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This review article has been produced in good faith, based on information and literature in the public domain and other available resources. While the information and opinions given are sound, all parties must rely on their own skill and judgement when making use of it. To the best of the authors’ knowledge, the information contained in the report, including drafted figures, does not infringe any copyright or contain any protected intellectual property. However, no warranty is provided for the accuracy of the content or unforeseen copyright infringement should this document, or parts of it, be published or relied upon. The Supergen Bioenergy Hub and BBNet will not assume any liability to anyone for any loss or damage arising out of the provision of this report.

The full report which this review informed can be found online. All enquiries related to this publication should be sent to: supergen-policy@aston.ac.uk.

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