# Biopolymers (bio-based plastics) – An overview
## Author: Professor Callum Hill (JCH Industrial Ecology Ltd)
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The carbon atoms in biopolymers are derived from biogenic (photosynthetic) sources. Biopolymers can be encountered in nature (e.g. cellulose, starch, lignin), or they can be produced from bio-based feedstocks (e.g. poly(lactic acid) (PLA), bio-polyethylene (bio-PE)). Although biological in origin, a biopolymer does not necessarily break down by natural processes in the environment. For example, bio-PE is identical to poly(ethylene) derived from fossil resources and will persist for the same length of time in the environment.

At the present time, biopolymers do not have significant market share and for this to change, the following requirements will have to be met:

- Continued technological progress in the bioprocessing phase
- Significant progress in downstream processing technologies
- Fossil fuel prices must be high (this will be less important as the production technologies for biopolymers mature)[1]
- The price for fermentable sugar must be low, or there is a breakthrough in the utilisation of lignocellulosic biomass

With the fall in oil prices in recent years, companies producing bio-based feedstocks have re-focussed activities on high profit, low volume areas:

- Food and nutrition, flavours, fragrances, cosmetics
- Pharmaceuticals, fine chemicals
- Bio-based drop-ins for niche markets.

Nova Institute have estimated that the potential production capacity for biopolymers in Europe is around 1.3 million tonnes per year by 2020 (Table 1). The global production of biopolymers was just over 2 million tonnes in 2017 and is predicted to reach 2.44 million tonnes by 2022.[2] The main market segments for biopolymers (2017) are rigid and flexible packaging (both short life products) (Table 2).

| Table 1. Production capacity for biopolymers in Europe, current and projected | | |
|---|---|---|
| Bio-Polymer | Production capacity 2011 (t/a) | Production capacity 2020 (t/a) |
| PLA | 8,220 | 226,730 |
| Starch blends | 217,000 | 539,000 |
| PHA | 50 | 10,090 |
| Polyamide | 16,000 | 31,000 |
| PBAT | 74,000 | 74,000 |
| Polyolefins | 0 | ? |
| PET | 0 | 300,000 |
| PBT | 0 | 80,000 |
| PUR | 39,450 | 39,450 |

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[1] Or equivalent outcome e.g. though upstream carbon pricing or other policy intervention.
[2] European Bioplastics, https://www.european-bioplastics.org

| Total | 354,720 | 1,300,270 |
|-------|---------|-----------|
| **Source:** Nova-Institute GmbH (2013) Production Capacities for Bio-based Polymers in Europe – Status Quo and Trends towards 2020 | | |

| **Table 2.** Global bio-polymer production, by market segment, 2018 | |
|------|------|
| Market segment | Quantity (tonnes) |
| Rigid packaging | 699,500 |
| Flexible packaging | 518,000 |
| Textiles | 239,000 |
| Automotive and transport | 155,000 |
| Consumer goods | 143,500 |
| Agriculture and horticulture | 119,500 |
| Coatings and adhesives | 102,500 |
| Building and construction | 76,500 |
| Electrical and electronics | 34,000 |
| Others | 21,000 |
| **Total** | **2,108,500** |
| **Source:** European Bioplastics, https://www.european-bioplastics.org | |

The GHG mitigation potential of biopolymers derived from biomass arises due to sequestration and storage of atmospheric carbon in biopolymer products and the potential for a reduced Global Warming Potential (GWP) impact when substituted for fossil-derived alternatives.[3]

**The benefits in term of carbon storage are limited in packaging as these are typically short-lived products**:

- Of the market segments listed above, only automotive/transport and building/construction applications are likely to have product lives in excess of a few years. The top three categories will have product lives less than a year and consequently the product pool is unlikely to significantly exceed the annual production capacity.
- The fact that products are short-lived limits the total size of the carbon store. The approximately 2 million tonnes of biogenic carbon currently in the global biopolymer product pool (equivalent to 7.3 million tonnes of $CO_2e$) represents a mere 1.5% of the UK annual emissions and 0.02% of global emissions.
- This is a one-time carbon sink occurring while the products' pool is filling, but it is in equilibrium thereafter (i.e. it is a carbon store and not a sink). If the products' pool decreases then it effectively becomes a source of atmospheric carbon.

The mitigation potential can be determined with a consideration of the UK polymer sector. In 2015 the UK produced 1.7 million tonnes of polymer. Roughly 60% of these polymers were used in short-life applications, such as packaging, for which a maximum lifetime of one year is assumed. The remainder were used for longer life products, such as automotive (10 years lifetime assumed) and building products, for which a lifetime of 20 years is assumed. For the pools containing longer life products

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[3] i.e. the production of a functional unit of a biopolymer may have lower associated GHG emissions compared with the production of the same functional unit of a fossil-derived equivalent).

a loss of material based upon a distribution of 10(+/- 5) years and 20 (+/- 5) years was assumed (with total oxidation of the stored carbon at the end of product life). Two scenarios were considered: (a) a linear growth of market share by biopolymers of 0.5% per annum and (b) a growth of market share of 1.0% per annum (from a starting point of zero in 2020). The total market share for biopolymers was 15% and 30% in 2050, in scenarios a and b, respectively. The sequestered atmospheric carbon dioxide in 2050 is between 0.2 and 0.4 Mt $CO_2e$ (Fig. 1). However, this quantity is dependent on the growth in market share.

Figure 1: Sequestration of atmospheric carbon dioxide due to increase in biopolymer share of the UK polymer sector, with annual growth rates of 0.5% and 1.0%
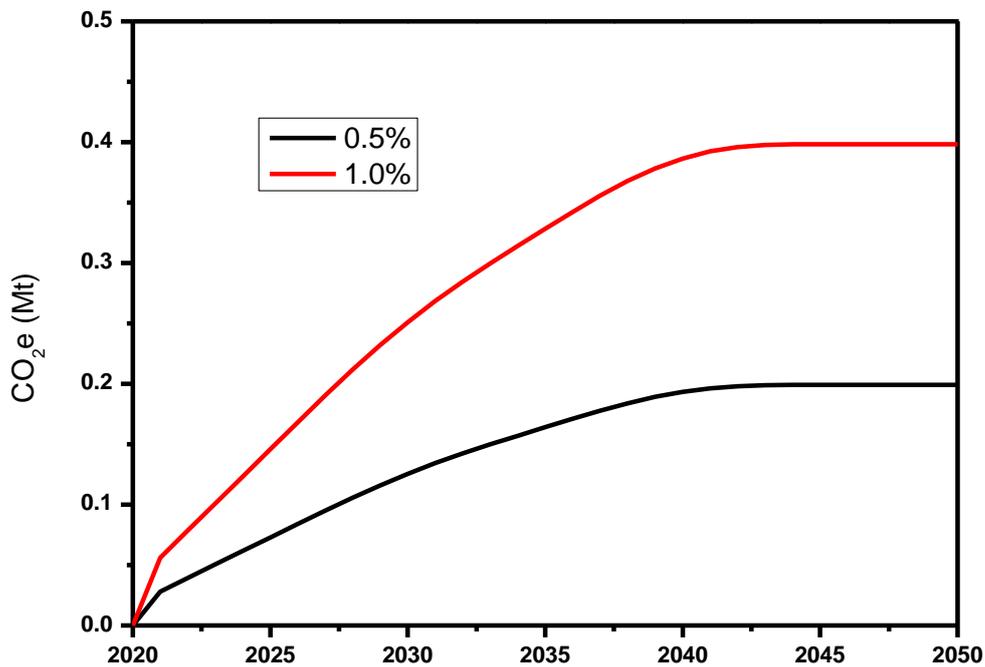


Any significant GHG mitigation benefit of using biopolymers therefore has to rely upon reductions in GWP impact due to substitution.

**GHG impacts of bio-based polymers (LCA studies)**

The biopolymer sector has the potential for producing materials with a reduced global warming potential (GWP) impact; compared to a functionally equivalent fossil-resource based polymer, with the GWP impact dependent upon the following factors:

- GHG emissions associated with the agronomy, or forestry practices and accounting for a potential land use change

- Whether there is any advantage to be gained in terms of a reduced GWP impact when using biogenic rather than a hydrocarbon-based polymer (substitution effect) - this applies for the manufacturing stage (cradle to gate[4]).
- Whether the biopolymer has the same functionality as the hydrocarbon-based alternative (mass substitution ratio).
- What the end of life fate is - especially if landfill is considered an option. The potential for emission of methane from landfill may be a significant negative factor.

Many lifecycle assessment (LCA) studies report on the manufacture stage of the life cycle only (the cradle to factory gate stage), which is necessary data to use as an input into the carbon storage models used in this study. However, **any consideration of the GWP benefits of using different materials has to take account of the entire life cycle** and as such, the results are heavily dependent upon the assumptions made regarding the in-service phase and especially the end-of-life phase, where there are many variables that may be taken into account:

- Recovery of plastic – energy recovery, mechanical recycling, feedstock recovery
- Alternative disposal scenarios – landfilling, incineration, composting, anaerobic digestion
- Energy recovery in the case of incineration
- Degree of degradation in a landfill
- Extent of $CO_2$ emissions vs. methane in landfill or during composting
- Whether the methane is recovered with flaring or with energy recovery.

Unfortunately, combining all stages of the life cycle in a single analysis does not always provide sufficient information to help with decision-making. For this reason, Rabl et al. (2007) recommend that the removals and emissions of GHGs (in $CO_2$ eq.) should be explicitly reported for each stage of the life cycle, as is the methodology adopted in the European Standard EN 15804. A search of the peer review literature and other published sources was undertaken to determine what the GWP impact of biopolymers was, compared to the fossil-derived equivalent materials, where appropriate (Figure 2). Most of the data are for cradle to gate, but some are for cradle to grave (indicated by the black boxes). There are significant uncertainties identified across the LCA literature (Box 1).

Figure 2: Global warming potential for bio-polymers and hydrocarbon-based polymers

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[4] i.e. not including operational and end of life.
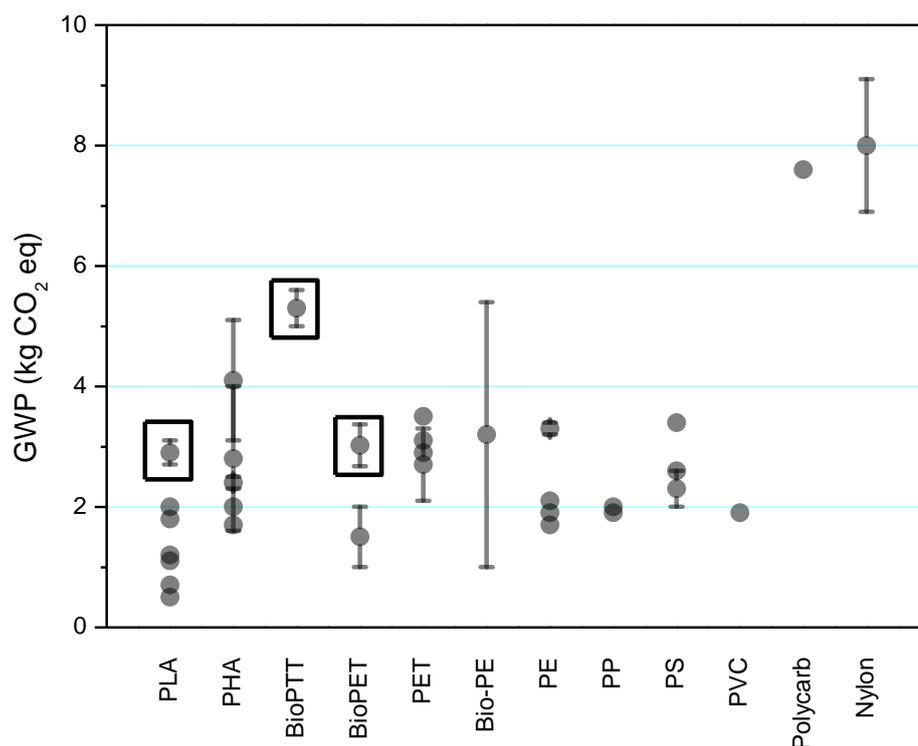
**Source**s: Akiyama et al. (2003), Broeren et al. (2016), Gerngross (1999), Gironi and Piemonte (2011), Heyde (1998), Hottle et al. (2013), Kendall (2012), Khoo et al. (2010), Kim and Dale (2005), Kurdikar et al. (2000), Liptow and Tillman (2009), Madival et al. (2009), Patel et al. (2006), Plastics Europe, Tsiropoulos et al. (2015), Vink et al. (2003), Vink et al. (2010), Yates and Barlow (2013).

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**Box 1. Uncertainties in LCA of biopolymers**

The environmental benefits of substituting biopolymers for fossil-based equivalents are not clear-cut, for example it has been suggested that cradle to grave LCA underestimates the landfill methane emissions associated with PLA (Krause and Townsend 2016). A biodegradable material disposed of to landfill may decompose anaerobically to release methane, which is a more powerful GHG than $CO_2$. This methane may be released directly to the atmosphere, it may be captured and flared off to produce $CO_2$, or it may be captured and used to produce energy. In the latter case, GWP credits would apply depending upon the energy source being substituted. Complete degradation in the landfill may not occur, or may occur at different rates depending upon conditions; this fate has to be modelled in the LCA and this has to rely upon degradation data which may be lab-based and not properly reflect the true conditions operating in the landfill. Incineration at end of life may be a preferred option and this may occur with or without energy recovery, thereby affecting the overall GWP impact associated with the whole life cycle. Some studies even assume that landfilling is a preferred option, since this ensures long-term carbon storage, but a study of the end of life options for bio-plastic bags, landfill was considered to be the least desirable scenario compared to incineration or composting (Khoo and Tan 2010). Van der Harst and Potting (2013) compared the LCAs of disposable cups made from different materials, focussing on GWP. The

LCA data was strongly influenced by the end of life assumptions; for example, the GWP of a paperboard cup was ten times higher if complete degradation in a landfill was assumed rather than no degradation (depending upon the quantity of methane generation assumed and the assumed fate of this GHG).

For studies of the substitution of hydrocarbon-based polymers with bio-derived materials, it is vitally important to ensure that comparisons are made on a functional unit (FU) basis. For example, Shen et al. (2012) compared the embodied energy and GHG emissions associated with the production of a partially bio-based PET, PET, and PLA water bottle. It was found that there was a reduction in embodied energy and GHG emissions if PLA was used instead of PET, assuming the same weight for each polymer for the FU. However, it was considered most likely that the FU would require approximately double the weight of PLA, in which case the environmental benefits were negligible. Consideration also has to be given to land use change (LUC), if this is a factor in the production of a feedstock for the biopolymer. Suwanmanee et al. (2013) compared thermoform food boxes made from polystyrene, PLA, or PLA/starch blend in a cradle to gate LCA, which included LUC emissions associated with the production of the renewable feedstock. It was concluded that the PLA and the PLA blend both had a higher environmental impact compared with the PS only product, when LUC was taken into consideration.

The GWP data presented in this report represents the current state of the art and it is very likely that reductions in impact for the cradle to gate life cycle stage will be observed as the technologies mature Vink et al. (2010).

Based upon the current published LCA data, **the effectiveness of biopolymer substitution to act as an effective GHG mitigation strategy is unclear**.

**Conclusions**

When analysing the potential for the use of feedstock chemicals for biopolymer production, it is necessary to consider the constrained availability of land placing limits on total production (Bos et al. 2012), a major consideration in a UK context. In 2016, 132,000 ha of agricultural land were used to grow crops for bioenergy (Source: DEFRA 2017), of which about 70,000 ha was used to produce biofuels for the UK road transport sector. Approximately 195 million litres (154,000 tonnes) of ethanol were produced in 2015/16 (source: DEFRA), using 50,000 ha of arable land (source: DEFRA); resulting in an apparent ethanol productivity of about 3 tonnes ethanol per hectare.

| Table 3. UK bio-ethanol production capacity | | | |
|---|---|---|---|
| **Owner** | **Location** | **Capacity tonnes p/a** | **Feedstock** |
| Ensus | Yarm, Teesside | 316,000 | Wheat |
| Vivergo | Hull | 332,000 | Wheat |
| British Sugar | Norfolk | 64,000[a] | Sugar beet |
| **Source**: Defra, 2017 **Notes:** [a] Converted to biobutanol | | | |

What, therefore is the theoretical potential to substitute the planned UK ethylene production capacity with bio-ethanol derived ethylene? Given the current UK bio-

ethanol annual production capacity of around 700,000 tonnes, equivalent to approximately 430,000 tonnes of ethylene, this would represent about 16% of the total UK ethylene production, containing 370,000 tonnes of biogenic carbon, equivalent to approximately 1.4 Mt $CO_2e$. According to the published data summarised in Table 4, the future UK production capacity of ethylene will be about 2.7 million tonnes (source: company published data).

| Table 4. Ethylene production UK | | | |
|---|---|---|---|
| **Owner** | **Location** | **Capacity tonnes p/a** | **Feedstock** |
| ExxonMobil | Mossmorran | 830,000 | Ethane |
| INEOS | Grangemouth | 1,000,000* | Ethane |
| SABIC | Wilton | 865,000 | Ethane |
| **Source**: Company published data **Notes:***Planned capacity | | | |

Assuming 100% conversion efficiency of ethanol to ethylene, this is equivalent to a demand of about 4.3 million tonnes of ethanol, which would require approximately 1.4 million ha of land (23% of UK arable land).

The potential for the production and use of biopolymers as a climate-change mitigation strategy in the UK is limited. Based upon the currently available LCA data, there is no clear-cut case for stating that there are benefits to be obtained by the substitution of a biopolymer for a functionally-equivalent fossil-derived material. This may change, as more sophisticated LCAs are undertaken on processes which have been optimised, but there are considerable uncertainties at present. The quantities of biopolymers used at the present time do not represent a significant pool for the storage of atmospheric carbon. Many polymeric materials are used in short-life products, such as packaging, which limits the time of carbon storage and hence the size of the carbon pool. There may be some potential for the use of bio-ethanol as a feedstock for ethylene production, but the economics have to be favourable and the demands on agricultural land in the UK would be significant, leading to displacement effects, such as increased transportation required to replace the foodstuffs not produced on these sites. There is some sequestration benefit where there is a growing market share for biopolymers. It is concluded that any potential mitigation benefits due to the use of biopolymers as a substitute for fossil-derived equivalents are unproven.

**Appendix 1: Polymer feedstock chemicals from bio-based resources**

There are several potential routes to the production of feedstocks for the production of polymers, of which bioethanol is the most advanced at this time in the UK, although this is currently used as a fuel rather than a platform chemical.

Bio-based polymers can potentially be produced from a range of different bio-derived feedstocks:

- C2: Ethanol, ethylene glycol
- C3: Lactic acid, 3-hydroxypropionic acid, glycerol, 1,2-propanediol, 1,3-propanediol
- C4: Succinic acid, 1,4-butanediol, 1-butanol
- C5: Levulinic acid
- C6: Sorbitol, 2,5-furan dicarboxylic acid, adipic acid

**Ethanol**

The most attractive option for the production of significant quantities of biopolymer is to produce a feedstock that can be used as a direct substitute in an already existing production process, with no requirements to modify the infrastructure. For this reason, the use of bio-ethanol as a platform chemical is attracting a lot of attention. The main product of interest is ethylene, synthesised by the dehydration of ethanol, but this is not presently commercially viable in the UK due to the high cost of bio-ethanol. In order for bio-ethanol to be a viable feedstock in the UK, it would have to be produced in sufficient volumes at a low enough cost. Bio-ethanol is produced by fermentation of glucose, which is obtained by acid hydrolysis of starch, or directly from sugar cane or sugar beet. This is known as 1G (first generation) glucose. Second generation (2G) glucose, which is obtained from lignocellulosic feedstocks, is not sufficiently pure to be used as a substrate for the production of bio-based chemicals at this time. However, Avantium (based in the Netherlands) is claiming that they have developed a process for producing high purity 2G glucose in a cost-competitive process.

Bio-ethylene is made by the catalytic dehydration of bio-ethanol using an alumina or silica-alumina catalyst. It is claimed that there is a saving of 60% in fossil energy when making bio-ethylene from sugarcane, when compared to petrochemically-derived ethylene and a reduction of 40% in associated GHG emissions, although there is a smaller saving if corn syrup is used as the feedstock. The GWP values for bioethylene production are also strongly influenced by the land use change scenarios associated with the ethanol production (Liptow and Tillman 2012, Liptow et al. 2013). In 2013 BP announced that it had developed a new lower-cost technology 'Hummingbird' for the production of ethylene from ethanol, which was subsequently acquired by TechnipFMC plcIt has been estimated that if all of the ethanol currently produced for the transport sector globally was used to manufacture bio-ethylene, this would supply about 25% of global demand (IEA-ETSAP 2013). Ethylene is a platform chemical for the production of many important polymers, including polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET).

To supply the total global capacity of ethylene in 2020 (200 million tonnes) would require 320 million tonnes of bioethanol, representing just over 100 million hectares. Bio-ethylene is produced in Brazil, China, India and Taiwan. The costs of bio-ethylene production are very strongly influenced by the feedstock ethanol costs (Mohsenzadeh et al. 2017). Global bio-ethylene production is currently around 0.5 million tonnes per annum.

## Ethylene glycol (EG)

Ethylene glycol, also known as monoethylene glycol (MEG) is a di-alcohol (diol) used for the production of polyester fibres and poly(ethylene terephthalate) (PET) resins. MEG is obtained by the hydrolysis of ethylene oxide which is in turn made by the oxidation of ethylene. If bio-ethylene was the feedstock then this will yield bio-MEG, however Avantium, based in the Netherlands, have plans to build a pilot plant to produce bio-based MEG directly from sugars. Previously, the route to bio-MEG involved a four-step process, making the product uneconomic. Avantium have developed a one-step hydrogenation conversion process with high carbon efficiency. There are no plans for UK production at this time.

## Lactic acid

Lactic acid is produced by fermentation of glucose, molasses or starch hydrolysates. Lactic acid production globally in 2013 was just over 300,000 tonnes; it is not produced in the UK. The HGCA funded a study to investigate the potential for lactic acid production from UK cereal milling residues, which concluded that the although the technology was not sufficiently well developed to use these as a substrate, there was potential for exploring this feedstock (HGCA 2013, project report 536). The main use of lactic acid is for the production of poly(lactic acid) PLA, although lactic acid salts, lactate esters, acetaldehyde, acrylic acid, lactamides, 1,2-propanediol, propionic acid, 2,3 pentadione, oxalic acid and pyruvic acid.

## 3-Hydroxypropionic acid (3-HP)

This compound is not readily produced by chemical synthesis, but could potentially be produced by fermentation from glucose or glycerol. It can be used to produce the biodegradable polyester poly(3-hydroxypropionic acid), or converted into propanediol, malonic acid, acrylic acid, esters, or amides. Research into 3-HP fermentation at pilot scale has been conducted by Cargill and Novozymes.

## Glycerol (1,2,3-propanetriol)

Glycerol can be produced from hydrocarbon feedstocks from propylene via the intermediates allyl chloride and epichlorohydrin, but this source is decreasing with most glycerol being sourced from biomass where it is a by-product of biodiesel production. Glycerol can be used to make epichlorohydrin, acrylic acid, or propanediol. It can also be used to make polymers via glycerol carbonate, which is converted to glycidol and then polymerised to polyglycidol, or it can be used to synthesise alcohol epoxides, or it can be reacted to dimethyl carbonate as a feedstock for polycarbonates or polyurethanes. The problem with crude glycerol from biodiesel production is that it is contaminated with methanol and has a high salt and

free fatty acid content (Ciriminna et al. 2014), this has tended to limit its use in higher value applications. It is used as an additive to cattle feed because the animals can tolerate relatively high levels of methanol. Crude glycerol can also be used as a cement additive. Glycerol can be added to anaerobic digesters as a source of carbon. Bi-on and Greenergy International Ltd. Have recently signed an agreement to study the possibility of producing PHA from glycerol and establish the feasibility of building a 5,000 tonne per annum pilot plant in the UK. There are currently three biodiesel plants operating in the UK: Bio UK Fuels, Argent Energy UK and Uptown Biodiesel, all using waste cooking oil as the feedstock, oilseed rape was last used to produce biodiesel in 2014. According to the UK Government RTFO Year 10 report, it was estimated that 375 million litres of biodiesel (FAME) were consumed in the financial year 2017/8. Used cooking oil supplied 141 million litres of the total UK production of 193 million litres of biodiesel in 2016/7, with most of the remainder coming from tallow and food waste (Source: DEFRA). It is estimated that the amount of used cooking oil available in the UK from catering and food manufacturers is 130-270 thousand tonnes and could be as much as 260-410 thousand tonnes if the domestic sector was included (Ecofys 2013), this would yield between 15-48 thousand tonnes of glycerol. If this was used to make polymers for short life products as packaging (as is likely), then this represents and insignificant atmospheric carbon sink. Assuming the UK meets the EU obligation arising from the Renewable Energy Directive, it will require approximately 6 million tonnes of biofuel in 2020. The land use requirements to supply this fuel could increase from the current 1.4 million ha to between 4-8 million ha depending on the feedstock used (Joint Nature Conservation Committee 2009).

**1,3-Propanediol (PDO)**

PDO is produced by Shell from ethylene oxide via hydroformylation to 3-hydroxypropionic aldehyde in an 83 ktonne p/a production facility in Geismar, Lousiana. PDO can be used as a precursor for the polymer poly(trimethylene terephthalate) (Kurian 2005). Propanediol can be produced by fermentation of glycerol (Glory Biomaterial, Shenghong Group, METEX, Technip). Metex has announced plans for a 47 ktonne per annum plant to produce PDO for the cosmetics market. Dupont and Tate and Lyle have developed a process to manufacture PDO from a glucose feedstock located in Louden TN USA with an annual production capacity of 63.5 kt, which they claim has a cradle to gate GWP 56% lower than the petrochemical route. PDO is a component of industrial bio-polyesters, where it is combined as a co-monomer with terephthalic acid or dimethylterephthalate for the manufacture of poly(trimethylene terephthalate), such as DuPont's Sorona®, CPD Natureworks®, or Shell's Corterra™.

**Succinic acid (SA)**

This is usually made by the catalytic hydrogenation of petrochemically-derived maleic acid or maleic anhydride. Total bio-SA capacity is 60 ktpa, with four companies dominating the market BioAmber with a 30 ktpa plant in Canada and a 36 ktpa plant planned for China, Myriant with a 14 ktpa plant in the USA, Reverdia with a 10 ktpa plant in Italy and Succinity with a 10 ktpa plant in Spain. Succinic acid can be used as a precursor to 1,4-butanediol by a hydrogenation route. SA can also be used to replace adipic acid in polyester polyols (for polyurethanes), lubricants,

saturated polyester resins, to replace phthalic anhydride or isophthalic acid in unsaturated polyester resins, alkyd resins, plasticisers, or replace isophthalic acid to make PET polymer. There have been only two LCA studies of bio-succinic acid production (Pinazo et al. 2015, Moussa et al. 2016).

## 1,4-Butanediol (BDO)

BDO is a versatile chemical intermediate, with a global production capacity of 2.5 million tonnes pa. Genomatica has developed a non-SA route, which is used by DuPont, Tate and Lyle and Novamont and is licensed to BASF. Novamont opened a 30 ktpa plant in Italy in 2016 and BioAmber has plans for a 70 ktpa SA-based butanediol plant. Butanediol and its derivatives are used for producing plastics, solvents, electronic chemicals and fibres.

## 1-Butanol

The industrially important routes to 1-butanol are propylene hydroformylation, Reppe synthesis and crotonaldehyde hydrogenation, with annual production in the region of 1 million tonnes per annum. There is interest in the fermentative production of 1-butanol from biomass, with a focus on reducing the feedstock costs, increasing the yields, improving downstream processing and product recovery and improving the long-term stability of the process. The main uses for 1-butanol are as a solvent and applications as plasticisers (butyl esters of phthalic, adipic, sebacic, oleic, azelaic, stearic and phosphoric acids). The BP and DuPont joint biobutanol pilot plant in Saltend was mothballed in 2016. There is currently no commercial UK production.

## Levulinic acid (LA)

LA is only produced in small quantities globally at present, by the acid-catalysed carbohydrates in small scale batch reactors. It can be converted to:

- Diphenolic acid by reaction with phenol – which has the potential to replace Bisphenol A in polycarbonate production
- 1,4-pentane diol by hydrogenation
- Succinic acid by oxidation
- Acrylic acid by oxidation

The exploitation of levulinic acid is being researched by Avantium.

## Sorbitol

Sorbitol is produced in industrial quantities (in excess of 1 m tonnes pa) by the catalytic hydrogenation of glucose. Sorbitol can be polymerised to form poly(etherpolyols) which can be used as intermediates for the synthesis of polyurethanes. Hydrogenolysis of sorbitol leads to propylene glycol, which is used as a building block for unsaturated polyesters.

## 2,5-furan dicarboxylic acid (FDCA)

FDCA can be obtained in a single step oxidation of hydroxymethyl furfural, which can be obtained by acid treatment of inulin, starch or fructose. The potential for furan-based building blocks to be used for polymerisation have been extensively reviewed by Gandini et al. (2009).

**Adipic acid**

Adipic acid is the most important aliphatic dicarboxylic acid commercially and is usually derived from the nitric acid oxidation of a cyclohexane, an inefficient process that releases $N_2O$, a potent greenhouse gas. The Dupont adipic acid plant in Wilton developed a process to capture the $N_2O$ and react it with methane to produce nitrogen, $CO_2$ and water, with the excess heat being used to generate process steam. The plant closed in 2009. A route from tetrahydrofuran 2,5- dicarboxylic acid (derived from renewable bioresources) has been presented (Gilkey et al. 2017). Adipic acid is used in the manufacture of nylon-6,6 polyamide.

**Biopolymers**

There are two categories of biopolymers, those which are polymers in the natural environment (e.g., starch, pectins, cellulose, lignin) and polymers which are derived from bio-based feedstocks. In the latter case, the polymers may be identical with petrochemical derived polymers (e.g. polyethylene and bio-polyethylene). Although some biopolymers will break down in the natural environment, this is not always the case. There is some limited production of cellulosic and starch-based materials in the UK.

**Cellulose**

Pure cellulose can be used as a source of glucose after acid hydrolysis. However, cellulose is relatively resistant to such treatment due to its highly crystalline nature. However, lower levels of hydrolysis can be used to release cellulose whiskers, which have the potential to be used as reinforcement elements in nano-composites. Cellulose can by chemically modified to produce more easily processible materials, or it can be regenerated to form films or fibres. Lenzing in Grimsby have a plant producing Tencel fibres from cellulose sources, with an annual capacity of 45,000 tonnes. Cellulose fibres derived from recycled paper can also be used as insulation materials, which represents a relatively long-term carbon store of over 50 years, but the quantities involved are very small at present.

**Starch**

Starch-based polymers are a well-established technology. Starch can also be used as a feedstock for glucose by acid hydrolysis. Approximately 80% of bio-based polymers are manufactured from starch, which is obtained from many crops, which can also be used as food crops.  When used as a biopolymer material, starch is invariably plasticised. Many modifiers have been used to plasticise starch including; glycerol, sorbitol, water, urea, ethanolamine and formamide. For many processing applications thermoplastic starch is required. Production capacities of starch blends in Europe are expected to be just over half a million tonnes by 2020 (source: Nova Institute). The British starch industry extracts approximately 800,000 tonnes of starch from cereal grains (700,000 tonnes of UK wheat and 750,000 tonnes of maize, principally from France) and processes it in to a great many products, from native starches, to physically modified starches, liquid and solid sugars (principally in the form of glucose syrups and isoglucose) for food and non-food uses. The bulk (about 70% by weight) of the industry's production is sweeteners. There are four starch producers in the UK:

- Cerestar A Division of Cargill
- National Starch & Chemical
- Roquette UK Ltd
- Tate & Lyle Food and Industrial Ingredients

**Lignin**

Lignin is the second most abundant polymer on Earth. The aromatic structure of the lignin macromolecule potentially makes it a promising feedstock for bio-based

chemicals. However, the complex structure of lignin makes the separation, isolation and purification of useful phenolic compounds technically economically challenging. Lignin is commercially derived from two main chemical pulping processes:

- The kraft process, which uses the high lignin content black liquor wastes as an integral part of the energy and chemical recovery process. The lignin is available in a highly condensed (and hence unreactive) form and heavily contaminated with sulphur.

- The bisulphite process is used at the Borregard biorefinery in Norway. Lignin residues from such sulphur-based chemical pulping processes are contaminated with sulphur compounds which makes separation and purification difficult. Soda pulping processes of grassy feedstocks can produce relatively uncontaminated lignin feedstock streams. Other potential sources include organosolv pulping, steam explosion pulping and ammonia fibre explosion (AFEX) pulping (Conde-Mejía et al. 2012). There is also research interest in the use of ionic liquids, although the technical and environmental issues surrounding this technology are not yet solved. There is currently no chemical pulping process located in the UK.

Lignin is often used as an energy source in biorefining processes and in LCA studies of bio-derived chemical feedstocks, which improves the environmental profile of the process. Hence, using lignin for chemical or materials purposes would require the sourcing of an alternative energy feedstock, which may result in a greater environmental impact overall.

## PLA

Polylactic acid is derived from lactic acid which is obtained by the fermentation of corn starch.

A feasibility study by the National Non-Food Crops Centre for DEFRA suggested that it would be possible to manufacture 132,000 tonnes of PLA using 490,000 tonnes of wheat in the UK by 2025[5]. The HGCA considered this entirely feasible since 3.9 million tonnes of wheat are exported annually from the UK. According to Natureworks, approximately 2.5 kg of US maize grown on $2m^2$ of land is required to produce 1 kg of PLA. There is no UK production at present.

PLA is not currently recycled, although mechanical recycling is being studied as the preferred option (Soroudi and Jakubowicz 2013), but there are insufficient volumes of PLA in use to justify setting up the infrastructure. Although amorphous PLA will biodegrade, it is noted that semi-crystalline PLA will not anaerobically degrade at 35°C.

## PHA

Poly(hydroxyalkanoates) are produced in nature by many organisms, including bacterial fermentation of sugars. There are a wide range of PHAs with different

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[5] Industrial uses for crops: Bioplastics (HGCA) (2009)

material properties. An industrial process for producing PHAs was developed by ICI in the 1980s, which was sold under the trade name Biopol. Kim and Dale (2005) compared the GWP impacts and embodied energy associated with the production of PHA using Metabolix fermentation technology and compared this to the data of Gerncross (1999) and Akiyama (2003). Kim and Dale (2005) calculated a sequestered carbon content in PHA of approximately 2 kg $CO_2e$ per kg of PHA, this value has been used to calculate GWP impact, when the sequestered atmospheric carbon is included in the reported figures.

### Bio-PET

Partially bio-based PET is made from bio-based ethylene glycol, which is obtained from bio-based ethylene, via ethylene oxide. This is currently produced in India. Bio-MEG represents 27.7% of the inputs (in mass) required for Bio-PET production, with the remainder being terephthalic acid, which is produced from para-xylene. So far, no commercial process for producing bio-derived para-xylene exists. It is more likely that PET in bottles will be replaced by PEF as a bio-based material. According to Tsiropoulos et al. (2015) the GWP impact of bio-PET production in India is heavily influenced by considerations of transport of ethanol and land use change, with savings of 3-11% being possible compared with petrochemical PET.

### Bio-poly(trimethylene-terephthalate) (Bio-PTT)

Bio-PTT is produced by the reaction of 1,3-propane diol with terephthalic acid, or dimethyl terephthalate. According to Álvarez-Chávez et al. (2012), production requires 20-50% less energy and the GWP impact is 44% lower than its PBP counterpart.

### Bio-polyethylene furanoate (PEF)

PEF is derived from corn-based fructose, with production divided into three main stages: extraction of fructose from corn starch, the conversion of the fructose to Furanics products with subsequent extraction and purification and the oxidation to furan-2,5-dicarboxylic acid and reaction of this with ethylene glycol (MEG). A study by Eerhart et al. (2012) showed that substituting PEF for PET would save 40-50% in embodied energy and approximately 45-55% in GHG emissions. This study also showed that bio-PEF had the lowest EE and GWP of all bio-based polymers in a broader study which included PHA, PLA and bio-PE.  There is currently a pilot plant operating in the Netherlands with a capacity of 40 tonnes per annum, owned by Avantium. Avantium have entered into joint development agreements with the Coca-Cola Company, Danone and ALP LA to develop and commercialise the production of PEF bottles.

### Bio-urethanes/polyols

There is a maturing vegetable oil-based polyester polyols market, as well as R&D in succinic acid-based polyols and some interest in bio-isocyanates. This might prove to be a better use for vegetable oils compared to biodiesel production, but this would require a properly constructed LCA to determine.

**Bio(polyethylene)**

According to Tsiropoulos et al. (2015) Bio-based polyethylene has an embodied GWP impact of approximately -0.75 kg $CO_2$e per kg of polymer, ranging from -0.55 to -0.88 kg $CO_2$e depending upon allocation approach. Posen et al. (2015) undertook a comparative LCA study examining the use of bioethanol as a fuel or as a feedstock for LDPE in a US context. They found that the results were strongly influenced by the choice of feedstock for bioethanol production. Bio-polyethylene derived from corn was found to have a higher GWP compared with sugarcane or switchgrass.

Liptow and Tillman (2012) undertook a comprehensive study of the embodied GWP impact of bio-PE compared with PE production using different bio-resources and different carbon accounting methods to report on the storage of atmospheric carbon in the product and also the soil. This gave a wide range of different values depending upon the model adopted. For the production of ethanol from wood chips as a feedstock for bio-ethylene, it was a found that enzyme production was a major contributor to the GWP impact.

**Appendix 2: The wider UK polymer industry**

In 2015 the UK produced 1.7 million tonnes of polymer and consumed 3.3 million tonnes of polymer (Tables 5 and 6).  (Source: British Plastics Federation).

| **Table 5.** Plastics utilisation by different markets (UK) | |
|---|---|
| Market | Percentage |
| Packaging | 44.3% |
| Building and construction | 23.6% |
| Other | 20.1% |
| Automotive | 6.6% |
| Electrical and electronic | 5.5% |
| **Source:** BPF | |

| **Table 6.** UK production of polymers | | | |
|---|---|---|---|
| Polymer | Company | Location | Production capacity (ktpa) |
| PE | INEOS Olefins & Polymers | Grangemouth | 330 |
| PE | Sabic UK Petrochemicals | Wilton | 400 |
| PP | INEOS Olefins & Polymers | Grangemouth | 285 |
| PP | Basell Polyolefins UK | Carrington | 230 |
| PET | Lotte Chemical UK | Wilton | 350 |
| PET | Indorama Polymers | Workington | 168 |
| PET | PET Processors | Dumfries | 20 |
| PVC | Innovyn | Newton Aycliffe | 300 |
| PVC | Vinnolit GmbH | Hillhouse | 45 |
| PMMA | Lucite International | Newton Aycliffe | 3 |
| PEEK | Victrex | Thornton Cleveleys | 7 |
| PTFE | Asahi Glass Fluoropolymers UK | Hillhouse | 3 |
| **Source:** British Plastics Federation | | | |

The polymer industry is part of the UK chemicals industry, which is one of the most energy-intensive industrial sectors in the UK, being responsible for 16.5% of total industrial energy consumption[6]. The chemical industry in the UK is growing at an annual rate of 1-3% and with no change in carbon emissions intensity, the sector could account for 11-13% of the UK total carbon budget by 2050. For the industry to reduce its carbon emissions by 80% by 2050, this would require an annual reduction in emissions intensity by 2-4% (Gilbert et al. 2013). Total GHG emissions from the UK chemical industry have reduced from 40 Mt $CO_2e$ in 1990 to 18.4 Mt $CO_2e$ in 2012, partly due to efficiency measures and also due to loss of production to overseas facilities.

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[6] Source: BEIS (2015) Industrial Decarbonisation and Energy Efficiency Roadmaps to 2050 - Chemicals

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