CROPQUEST

Bio Products Report

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Introduction

In recent years farm gate prices of agricultural commodities have stagnated. This has resulted in lower returns for farmers as the input costs of seed, fertiliser and labour have increased. By using crop products to develop alternative higher value products, greater economic returns to farmers can be achieved. These alternatives include speciality chemicals, polymers and products used in the pharmaceutical industry.

Targets outlined by the public private–partnership "bio–based industries" (BBI) include:

- To develop the potential of waste as well as of agriculture and forestry residues.
- To diversify and grow farmers' incomes: up to 40% additional margins with existing residues.
- To replace at least 30% of oil–based chemicals and materials with bio–based and bio–degradable ones by the year 2030.
- To create a competitive bio–based infrastructure in Europe, boosting job creation, 80% of which will be in rural and underdeveloped areas.
- To deliver bio–based products that are comparable and/or superior to fossil–based products in terms of price, performance, availability and environmental benefits.

The new bio–based products resulting from the BBI will on average reduce CO_2 emissions by at least 50% compared to their fossil alternatives.

With concerns about plastic waste problems, GHG emissions and oil price fluctuations provoking action from the public, businesses and households are moving towards more sustainable alternatives to conventional plastics (European Union, 2013).

Growing environmental problems and variable petroleum prices have attracted intensive research interest in the area of biopolymers (Peng et al., 2011). The markets for high value bio–based alternative products has a large potential for growth before a saturation point is reached.

The purpose of this report is to determine what high value products can be produced from crops that can or could potentially be grown in Ireland and to determine which products show the greatest promise for future development and investment.

Biopolymers

Poly lactic acid

Poly lactic acid (PLA), is an aliphatic polyester, produced through the polymerisation of lactic acid. The lactic acid is a product of the fermentation of sugars available from numerous annually occurring renewable feedstocks (van Groenestijn et al., 2008). Because annually renewable resources replace petrochemicals as the feedstock, PLA requires 20 – 50% less fossil resources than comparable petroleum-based plastics, depending on the plastic being replaced. PLA has similar characteristics to the petrochemically sourced polyethylene terephthalate (PET) with good transparency, glossy appearance, high rigidity, and ability to tolerate various types of processing conditions (Babu et al., 2013; Informa Economics, 2006). PLA can also be foamed and used to replace other polymers derived from petrochemicals such as polystyrene and polycarbonate for packaging purposes (Shen et al., 2010).

The two largest producers of PLA are NatureWorks (maize feedstock) and PURAC (cane sugar, potato starch and tapioca starch feedstocks) with a new company, Pyramid, recently commencing production of PLA in Germany (Shen et al., 2010). Two isomers of PLA can be produced depending on the strain of lactobacillus used during fermentation (Shen et al., 2010). The two types are L–lactide and D–lactide producing PLLA and PDLA, respectively. PLLA has a poor biodegradability score, while poly–DL–mixtures can be biodegraded within weeks under certain parameters (van Groenestijn et al., 2008).

The majority of the PLA consumed globally is a mixture of L– and D– lactides (>95% L–lactide, <5% D–lactide), which increases the melting point of the matrix (Shen et al., 2010). The current uses for PLA include film and tray packaging, bottle packaging and textiles. PLA has a low gas diffusion coefficient and is waterproof (van Groenestijn et al., 2008). Cargill's has a US patent application covering the fermentation of lactic acid from glucose in which a culture (reffered to only as a "homolactic acid-tolerant bacteria") is capable of growing at pH of 3.8 in the presence of 100 g L^{-1} of glucose, and producing nearly 100 g L^{-1} of lactic acid. At this reduced pH level, over 50% of the lactic acid is protonated, enhancing the recovery of the lactic acid for the subsequent process steps to poly lactic acid (PLA).

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) have gained a lot of attention in recent years due to the exhibiting properties of thermoplasticity and elastomericy along with PHA being biodegradable and biocompatible (Amache et al., 2013; van Groenestijn et al., 2008). Polyhydroxybutyrate (PHB), the simplest PHA, and one of the earliest plastics was discovered by Maurice Lemoigne in 1926. The generic process to produce PHA by fermentation involves bacterial fermentation, isolation, and purification from fermentation broth (Babu et al., 2013). PHB has similar material properties to polypropylene, with a good resistance to moisture and aroma barrier. As it is similar to polypropylene, PHAs can be processed in existing polymer processing equipment without the need for modifications. PHAs have received clearance from the FDA for use in food contact applications. These applications include caps and closures, disposable cutlery, kitchen knives, tubs, trays, and lids of disposable cups, and products such as housewares, cosmetics, and medical packaging (Babu et al., 2013). PHA biopolymers have also found applications in the food industry as food supplements and flavour delivery agents, as well as the medical industry for vascular grafts and stents (Amache et al., 2013).

The cost of raw materials, mainly carbon sources, is the most important factor affecting the overall economical competitiveness of PHA production. PHAs can be produced from molasses, which remains after the extraction of sugar from sugar beet. The molasses still contains a significant portion of sugar however it is uneconomical for processors to further remove the sugar resulting in the by-product. Jiang et al. (2008) used molasses from sugar cane as the growth medium for PHA production and achieved production rates of 22g L^{-1} using *Pseudomonas fluorescens* as the fermentation bacteria. A PHA yield of 94 g L^{-1} was achieved by Haas et al. (2008) using starch from potatoes as a substrate and *Ralstonia eutropha* as the producing microbe. Ahn et al. (2000) used cheese whey as a substrate for the production of PHA and achieved a production level of 96.2g L^{-1} using recombinant *Escherichia coli* cultures. Using molasses residues from sugar beet allows for PHA biopolymers to be produced while the sugar can be used for the production of more high value products such as biopharmaceuticals and fine chemicals. This would allow for the economical disadvantages of high feedstock costs to be overcome.

Polybutylene Succinate

Polybutylene succinate (PBS) is a biodegradable copolymer diester that can be made from 1,4–butanediol and succinic acid (Informa Economics, 2006). PBS already being made with petroleum-based succinate, is found in packaging film, bags, flushable hygienic products, and garden mulch (Potera, 2005). PBS generally has excellent mechanical properties and processability and can be applied to a range of end applications via conventional melt processing techniques, such as injection, extrusion or blown process (Adamopoulou, 2012).

PBS can also be used as an alternative to PET in bottles, polypropylene and polystyrene in some applications (Informa Economics, 2006). PBS is derived by combining succinic acid with 1,4–butanediol and subsequent polymerisation. Petrochemical methods of producing PBS involve electrochemical synthesis of chemicals such as acetylene and formaldehyde, however, fermentation of renewable sources as a method of production is becoming more popular (Babu et al., 2013).

Thermoplastic starch

Thermoplastic Starch (TPS) is a versatile biopolymer which can be obtained from renewable biological resources such as maize, wheat and potatoes. Starch consists of two component polymers, amylose and amylopectin (Shanks & Kong, 2012). TPS consists of a matrix of amorphous amylose and amylopectin produced through an extrusion process in the presence of a plasticiser, usually water and glycerol (Shanks & Kong, 2012; van Dongen et al., 2008). Depending on the level of plasticiser used during formation of the product the behviour of TPS ranges from soft and ductile to rigid and brittle.

As TPS is produced from native starch granules, the resulting product is biodegradeable (van Dongen et al., 2008). Blending of TPS with other biobased materials, results in products that can overcome shortcomings in pure TPS products. In mixed polymers the starch granules are added as a filler in the matrix without gelatinising the starch which reduces the overall cost of the product biopolymer product (Nafchi et al., 2013). Other materials, such as agrofibres and PLA, can be added to TPSs to increase the stiffness, shear strength and heat resistance of the polymers (Shanks & Kong, 2012; van Dongen et al., 2008).

TPS are mainly used in a film capacity for products such as shopping bags, bread bags, flushable sanitary products, mulch films and as a loose fill packaging material (van Dongen et al., 2008). Foamed loose fill packaging and injection moulded 'take away' food containers are applications of TPS with 50% of the market (van Dongen et al., 2008). TPS have a low migration coefficient for gases such as oxygen, carbon dioxide and water vapour, this makes TPS products an interesting choice for food packaging due to better conservation of the food products (van Groenestijn et al., 2008). Van Groenestijn et al. (2008) also report that margins for TPS production are low and this may limit the market potential of these products to areas with lower starch production costs.

Problems that occur with TPS are both water sorption and retrogradation, these cause the properties of TPS to change over time and under prevailing ambient conditions (Shanks & Kong, 2012). TPS foams are most suited to damping impacts and protecting fragile products including computer products and medical devices (Shanks & Kong, 2012).

Polytrimethylene terephthalate

PTT remained an obscure polymer for many years due to its relatively high cost, however, is now taking the transition from a traditional "specialty chemical" to a "commodity chemical" due to the recent advances in the synthesis of PTT from 1,3-Propanediol (Liu et al., 2010; Wu et al., 2002). The polymer now being synthesized via fermentation is a more economical process. PTT offers several unique properties as a polymer such as its force-elongation behavior, resilience and dyeing properties (Liu et al., 2010).

By using a modified strain of *Escherichia coli* bacteria, 135 g L^{-1} PDO was obtained with glucose as feedstock. This has resulted in a 40% reduction in the amount of energy required to make PTT. The production of bio-based PTT can reduce the formation of the toxic by-product acrolein more than 95% compared to traditional PTT. These energy savings compared to petro-based PTT have made bio-based PTT more attractive with good prospects for the future (Liu et al., 2010). PTT has found applications in apparel, upholstery, specialty resins, and other applications in which properties such as softness, comfort stretch and recovery, dyeability, and easy care are desired. The properties of PTT outperform both nylon and PET in fiber applications, and it surpasses polybutylene terephthalate and PET in resin applications such as sealable closures (Carole et al., 2004; Liu et al., 2010; Wu et al., 2002).

It was found that the average value of the Avrami exponent is about 2.8, and the work of chain-folding in the polytrimethylene terephthalate (PTT) crystalline phase is close to that of PBT but considerably lower than that of PET, indicating that PTT and PBT are more flexible than PET (Wu et al., 2002)

Chemicals

Ethylene

Ethylene, $CH_2=CH_2$, is the most widely produced organic chemical in the world. The major product is polyethylene commonly abbreviated as PE, is used to make hundreds of products including clothing fibres, where it is usually referred to as polyester, bottles and resins (AccessScience, 2014). Also as polyethylene terephthalate PET. Other important applications of ethylene include addition to poly(vinyl chloride), polystyrene, antifreeze (ethylene glycol), adhesives, solvents, and detergents (van Dongen et al., 2008).

Bioethylene is produced by the dehydration of ethanol derived from plant material (bioethanol) at elevated pressures and temperatures in the presence of an aluminium oxide (Al_2O_3) catalyst; the chemical formula for this process is $CH_3–CH_2–OH \rightarrow CH_2=CH_2 + H_2O$ (AccessScience, 2014). Most bioethanol is produced by fermentation of sugars from corn/maize (USA), sugar beet (Europe), sugarcane (Brazil), and sweet sorghum (China).

The production of Bioethylene based on sugarcane as a feedstock is estimated to save approximately 60% of the fossil energy compared to petrochemical production of ethylene as the process can also produce electricity. The production costs of sugarcane bioethylene are very low in Brazil and India (i.e. US$ 1,200 t^{-1} bioethylene) due to the low costs of sugarcane for the production of ethanol. Chinese production based on sweet sorghum is estimated at about US$ 1,700 t^{-1}. Higher costs are reported in the United States (from corn) and in the European Union (from sugar beets) at about US$ 2,000 t^{-1} and US$ 2,600 t^{-1}, respectively. This is due to the lower yields of sugar in the crop compared with sugarcane.

At present, the cost of lignocellulosic production is estimated at US$ 1,900 – 2,000 t^{-1} in the U.S. In comparison, the cost of petrochemical ethylene is substantially lower (i.e. US$ 400 – 1,300 t^{-1}, the price range over the last 10 years), depending on the region with a global average of US$ 1,100 t^{-1}. The current production cost of bioethylene is between 1.1 – 2.3 times higher than the global average petrochemical ethylene, but production of bioethylene from lignocellulosic sources is expected to reduce the gap in the near future (Broeren et al., 2013).

If all bioethanol currently produced for the transport sector (i.e. 61 million tonnes) was converted into bioethylene, this bioethylene would meet about 25% of current global demand. Projections suggest that bioethylene could meet between 40 – 125% of the global demand by 2035, depending on scenarios and taking into account co-products (Broeren et al., 2013). However, several industrial sectors (e.g. transportation fuels, power generation and the chemical industry) might compete for the availability of biomass feedstock reducing availability.

Moreover, starchy and sucrose biomass feedstocks alone cannot meet the total demand without competing with the food production industry (Dammer et al., 2103). As a consequence, the development of cheap and sustainable conversion processes of lignocellulosic biomass is crucial to increasing the basic resources of sustainable biomass (Broeren et al., 2013). Oil prices will also have a key impact on bioethylene market uptake (AccessScience, 2014). The prices for the production of conventional ethylene are based on prices for oil prior to the price collapse experienced in 2014/2015. This lower price for oil would make bioethylene less economically favourable.

As far as GHG emissions are concerned, to better reflect the environmental advantages of biomaterials, policy measures should account for life cycle emissions of products, not only the chemical sector on-site emissions occurring during the production process.

Table 1 shows that the production of ethylene from bio-based sources is not yet competitive with petrochemical sources. Table 1 shows the production costs of bioethylene using sugar beet as a feedstock is up to 3.5 times higher than using sugarcane in Brazil and up to 8.5 times higher than the petrochemical route.

Table 1: Overview of production costs of ethanol and ethylene from various sources[a].

Location	Feedstock	Ethanol Production cost		Ethylene Production cost	
		Mean	Range	Mean	Range
Starch / Sucrose feedstocks					
USA	Maize	800	690-1,070	2,060	1,700-2,730
Brazil	Sugarcane	420	360-560	1,190	970-1,630
India	Sugarcane	440	370-580	1,220	1,000-1,670
EU	Sugar beet	1,070	930-1,390	2,570	2,180-3,380
China	Sweet Sorghum	630	520-800	1,650	1,340-2,180

Lignocellulosic feedstocks					
USA	Biochemical	750	–	1,910	1,820-2,080
USA	Thermochemical	790	–	2,000	1,900-2,170
Reference production routes					
USA	Petrochemical	340	–	1,080	980-1,250
Global	Petrochemical	n.a	–	1,100	400-1,300

[a] All costs are in 2009 US$. Adapted from (Broeren et al., 2013).

Succinic Acid

A key chemical building block identified by Werpy and Petersen (2004) is Succinic acid which has a chemical formula of $C_4H_6O_4$. Succinic acid is a precursor to some specialized polyesters, primarily polybutylene succinate. It is also a component of some alkyd resins.

The main use of succinic acid is in the food and beverage industry primarily as an acidity regulator. Global production is estimated at 16,000 to 30,000 tonnes a year, with an annual growth rate of 10% (van Dongen et al., 2008). This growth rate can be attributed to advances in industrial biotechnology that seek to displace petroleum-based chemicals in industrial applications (Potera, 2005).
Succinic acid can also be sold as a food additive and dietary supplement, and is generally recognized as safe for those uses by the U.S. Food and Drug Administration. As an excipient in pharmaceutical products it is used to control acidity and, more rarely, in effervescent tablets (Potera, 2005). Succinic acid is also used as a building block for a number of other chemicals and was selected as a promising key building block chemical by Werpy and Petersen (2004). The products that can be derived from succinic acid are highlighted in Figure 1, which has been adapted from (Adamopoulou, 2012).

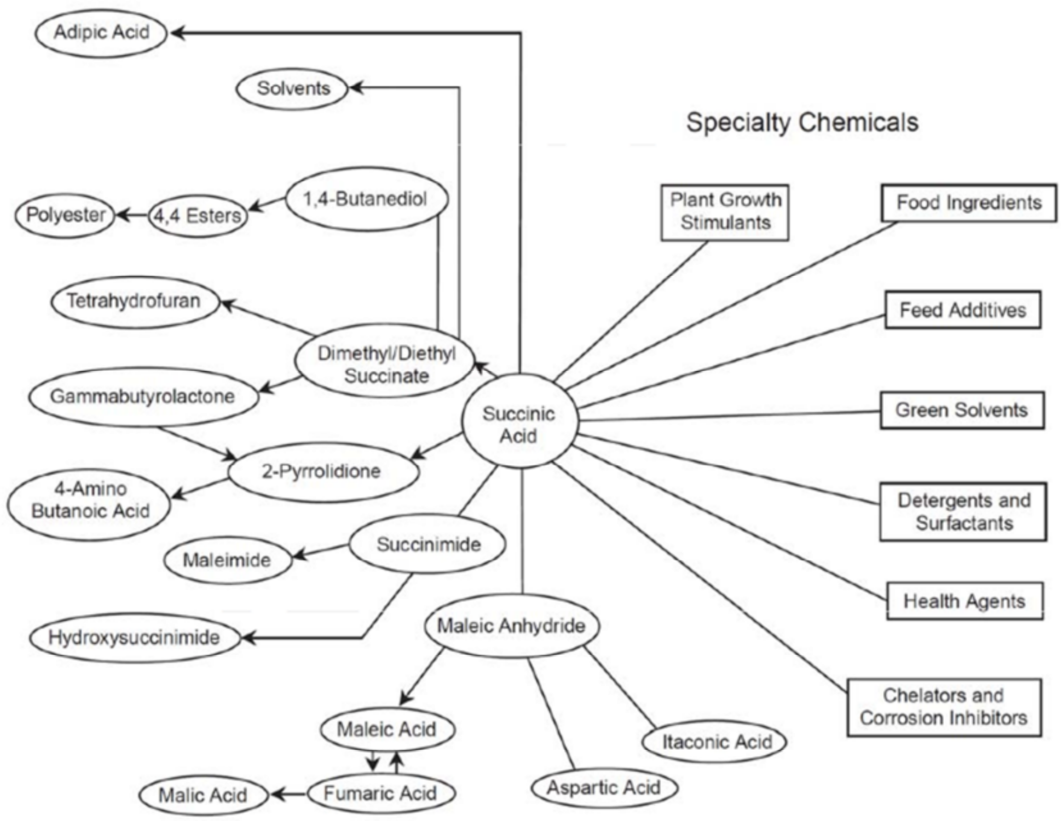

Figure 1: Products derived from succinic acid. Source (Adamopoulou, 2012).

Recently there has been growing interest in succinate-based runway and wing de-icer products. Succinate, which lowers the freezing point of water, replaces the formates and acetates in de-icers now on the market. These chemicals not only corrode the metal alloy, plastic, and rubber parts of airplanes, but also destroy the concrete surfaces and plastic and metal components of lighting equipment at airports (Potera, 2005). Other succinate based products under development include biodegradable solvents that do not cause air pollution or damage the ozone, a diesel fuel additive to reduce particulate emissions, and biodegradable polyesters for use in fabrics or plastics (Adamopoulou, 2012; Potera, 2005)

According to van Dongen et al. (2008) the potential turnover resulting from biobased succinic acid is €1,300,000,000 year^{-1} globally with €650,000,000 year^{-1} of this being in the EU. Figure 2 shows the primary markets that consume succinc acid and the economic sectors in which Ireland can play a role are highlighted. These sectors include the pharmaceutical, food, polymer and agricultural sectors

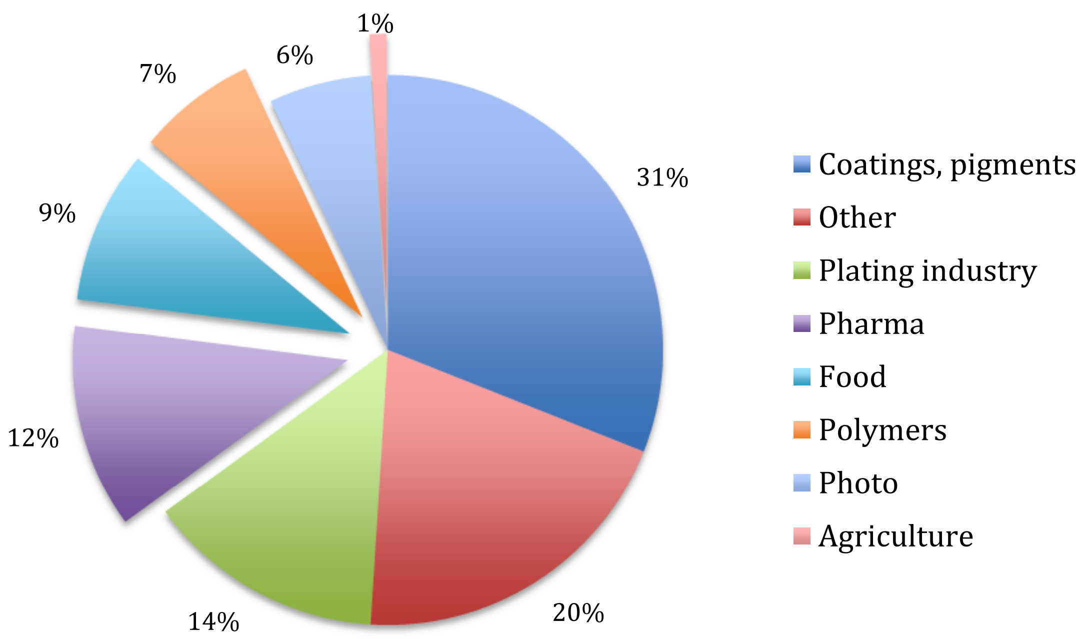

Figure 2: Potential applications for the use of Succinic acid with areas of particular interest for Ireland highlighted. Adapted from (van Dongen et al., 2008).

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Itaconic Acid

Itaconic acid is used globally in the industrial manufacture of resins such as polyesters, plastics, and artificial glass (Okabe et al., 2009). Werpy and Petersen (2004) has identified Itaconic acid a key building block for both the commodity and speciality chemical industries.

Itaconic acid is produced via fermentation with a strain of the fungus *Aspergillus terreus*. Itaconic acid is also known as methyl succinic acid and it is the methylated form of succinic acid (van Dongen et al., 2008). Itaconic acid can be used as a monomer in the production of acrylic fibre and as a pressure sensitive adhesive (van Groenestijn et al., 2008). A minimum productivity level of 2.5 g L^{-1} hr^{-1} must be achieved in order for Itaconic acid to be economically competitive (Werpy & Petersen, 2004).

According to Okabe et al. (2009) a significant problem in ophthalmic drug delivery systems is the retention of an adequate concentration of therapeutic agents in the pre-corneal area. Polycarboxylic carriers such as polyitaconic acid in a subcolloidal nanoparticulated hydrogel form have high potential uses in sustained drug release during ocular delivery. Another end use of Itaconic acid is in the production of synthetic latexes for improving the emulsion stability and adhesion (van Dongen et al., 2008). As reported by Okabe et al. (2009) more than 80,000 tons of itaconic acid was produced worldwide in 2009 and was sold at a price of around US$ 2 kg^{-1}. If lower cost fermentation based production of

Itaconic acid can be achieved it may enable itaconic acid to compete with the petroleum based chemical methyl methacrylate in the production of shatter proof glass replacements and clear plastics (examples of these include Plexiglass and Lucite). The markets for these products stood at roughly 680,000t year^{-1} with a price of €1.05 kg^{-1} in 2002 according to (van Dongen et al., 2008).

Calendula Compounds

A number of products can be obtained from either raw calendula oil or from the calendic acid which makes up ~60% of the oil profile. Alkyd paints with less volatile organic compounds (VOC) and non-fogging polyurethane foams can be produced from calendula oil as raw material, and their use would reduce VOC-emissions (Biermann et al., 2010). The main emissions of VOCs are caused by coating, printing ink, and adhesive processing techniques.

Biermann et al. (2010) reports that DSM have a patent which describes a resin composition containing a reactive diluent derived from the acid of an unsaturated vegetable oil such as tung oil or calendula oil serving as the solvent which is incorporated into the film while curing. Calendula oil can be used as a replacement for tung oil in a number of uses. As the global tung oil market is quite unstable a sustainable supply of calendula oil to processors particularly in Europe would be a strong advantage ensuring quality of the product and consistency of supply.

A review by Muley et al. (2009) has reported a number of pharmaceutical applications for extracts of Calendula. The ethyl acetate soluble fraction of the methanol extract of *Calendula officinalis* flowers exhibited both anti-inflammatory and antioedematous activities. Dichloromethane-methanol (1:1) extract of *C. officinalis* flowers exhibited potent anti-HIV properties. A methanol extract and 10 % decoction of the plant's flowers showed good potential anti-fungal and anti-bacterial properties. The ethyal acetate soluble fraction of the methanol extract of *C. officinalis* flowers has shown cytotoxic activity in *vitro* which is used in the treatment of leukemia. Other pharmaceutical uses of extracts of Calendula include: hepatoprotective activity; immunostimulant activity; antioxidant activity; spasmolytic and spasmogenic dual activity**.**

Biopharmaceuticals

The pharmaceutical industry plays an important role in the Irish economy. Of the top 10 global pharmaceutical companies, 8 are present in Ireland. The presence of the these companies helps make Ireland, according to IBEC (www.ibec.ie), the 7th largest exporter of pharmaceutical products in the world with a 2013 exports value of €50 billion. A number of products produced from bio-based products are used by the pharmaceutical industry. Bio-based products used in the pharmaceutical industry include both active pharmaceutical ingredients and products used to ensure proper administration of the active compounds within the body.

Exipients, including sugar and starch compounds, are used in the pharmaceutical industry for various functions including;

- Dilutants: enable accurate dosing of potent ingredients
- Binders to bind the tablet ingredients together giving form and mechanical strength.
- Disintegrants to aid dispersion of the tablet after consumption
- Coatings and films to protect tablet from the environment (air, light and moisture), increase the mechanical strength, mask taste and smell, aid swallowing and to assist with product identification (Augsburger & Zellhofer, 2006).

From an industrial biotechnological viewpoint, antibiotics provide the largest market share and this is expected to remain so until at least 2030 with the value increasing from €14 billion to €17 billion (Figure 3).

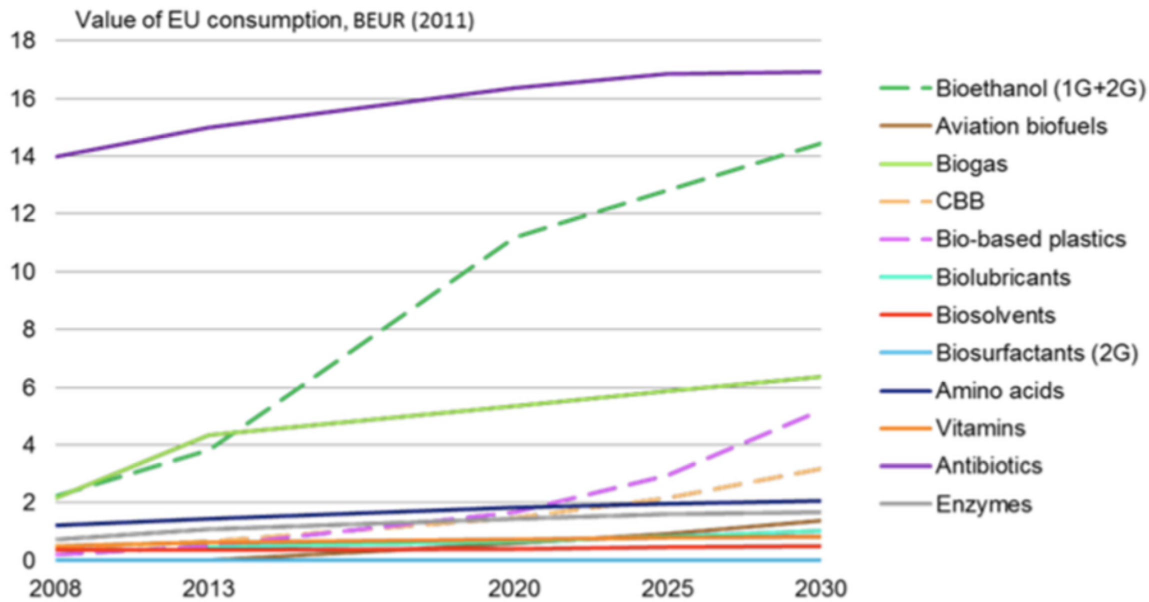

Figure 3: Estimated market demand by product segment in the EU up to 2030, Source; (European Union, 2013).

Antibiotics (including chloramphenicols, erythromycins, penicillins, streptomycins and tetracyclines) have the largest share of the biotechnology market as shown in Figure 3. Penicillin and cephalosporins are the two main antibiotics used for human and veterinarian purposes, however, a number of antibiotics are developed through fermentation techniques (Table 2). The removal of a side chain from cephalosporin results in the production of the compound 7–ACA of which the production volume is 4,000 – 5,000t year^{-1} (Zika et al., 2007). The production of cephalosporin antibiotics amounts to 30,000t year^{-1} for human and veterinary purposes with that of penicillins amounting to 45,000t year^{-1} (van Groenestijn et al., 2008).

In the case of 7–ADCA, another derivative of cephalosporin, the switch from chemical to fermentative synthesis has resulted in the use of 37% less electricity, 92% less steam, reduced wastewater by 90% and emissions of CO_2 have decreased by 75% (Zika et al., 2007).

Table 2: Selection of antibiotics used by the pharmaceutical industry and microorganisms used for production

Antibiotic	Microorganism
Cephalosporin	*Acremonium chrysogenum*
Chloramphenicol	*Streptomyces venezuelae*
Erythromycin	*Streptomyces erythreus*
Griseofulvin	*Penicillium griseofulvin*
Penicillin	*Penicillium chrysogenum*
Streptomycin	*Streptomyces griseus*
Tetracycline	*Streptomyces aureofaciens*
Gentamicin	*Micromonospora purpurea*

Recombinant human insulin was first introduced onto the biopharmaceutical market in 1982. Since its introduction it has replaced 70% of the insulin that is obtained from bovine and porcine pancreas'. The number of patients suffering from diabetes, globally, is expected to rise to 330 million by 2025 due to increasing levels of obesity (Zika et al., 2007).

Biological means can also be used to produce vaccines which represent an increasingly important prophylactic medical approach to dealing with diseases. Vaccines represented a minor role in the pharmaceutical market in 2005 at just 1% of the market (Zika et al., 2007), however this still amounted to €563 million. The EU is a major producer of vaccines with 52% of the market share. The majority of recombinant vaccines are produced to treat people for hepatitis b which infects 6% of the global population (Zika et al., 2007).

The production of biopharmaceuticals from fermentative procedures should fit strongly within the Irish economy due to the presence of large pharmaceutical companies, strong understanding of the pharmaceutical process, highly skilled and trained workforce along with a strong sugar beet production history (pre-2006) for the production of the feedstock required.

Agrofibres

Agro fibres are any fibrous material, which can be obtained from a crop. These include traditional sources of fibre such as jute, flax and hemp.

Typical fibres such as hemp and flax have a morphology with a lumen in the centre (Sfiligoj Smole et al., 2013), this allows for reduced bulk density, and high acoustic and thermal insulation properties. This makes agrofibres suitable for applications that require lightweight composites for noise and thermal automobile insulators (Sfiligoj Smole et al., 2013; Shahzad, 2012).

Hemp fibres have a higher modulus of elasticity and lower moisture absorption, and resist decomposition in alkaline environments better than other cellulose fibres (Sfiligoj Smole et al., 2013; Shahzad, 2012) making hemp more suitable for use in fibre/cement composites (Jarabo et al., 2012). Fibres from hemp can be used as reinforcement fibres for the production of roofing products as is discussed in Jarabo et al. (2012). The low density of the fibres allows for lower weight products to be devloped while maintaing the strength of the material.

Bast fibres (from plants) have also, in recent years, been used as a composite material in the production of polymers. Polymer composites have been found to be superior to those of the unreinforced materials. (Sfiligoj Smole et al., 2013).

A major disadvantage of cellulose fibres is their highly polar nature which makes them in-compatible with non-polar polymers. Another disadvantage is the low processing temperature that fibres are processed at. Only thermoplastics whose processing temperature does not exceed 230C, for example, polyethylene and polypropylene are useable in conjunction with natural fibres. Other thermoplastics like polyamides, polyesters, and polycarbonates, that require processing temperatures of greater than 250C, cannot be used with natural fibers (Shahzad, 2012).

According to Shahzad (2012) hemp composites showed the best flexural strength properties (54MPa) which is comparable with glass fibre composites with a propylene matrix (60 MPa). The specific flexural strength of the hemp composites was also higher than the glass fibre composite at 36.5 for hemp compared to 24 for glass fiber.

Bast fibres of flax and hemp are suitable for insulation materials due to their thermal properties and some ecological features, i.e., biodegradability. In a study reported by Kymalainen and Sjoberg (2008) the thermal conductivity values of flax, hemp, stone wool, glass wool and cellulose fibres from wood were reported. This study found that the thermal insulation properties of flax and hemp were similar to glass and stone derived thermal insulators depending on the bulk density and method of insulation used (i.e loose fill or mat). The use of fibres in the production of materials for construction, i.e insulation and roofing materials, would allow for more ecological houses to be built. If varieties of hemp and flax that allow for high yields of both seeds and fibres to be harvested, high economic returns for farmers would be achievable.

Enzymes

Feed enzymes are developed to function as digestibility enhancers for a variety of nutrients, such as phytases for plant phytate degradation and release of phosphorus content, carbohydrases for carbohydrate degradation, etc.

The worldwide feed additives market is estimated at about EUR 4.8 billion, including amino acids, vitamins, minerals, antibiotics, enzymes and acidifiers.

Baking industry:
Presently, enzymes are used to make up for deficiencies in some flours; to provide for specific properties in the flour and dough on a predictable basis; or to lower the protein level of flour for biscuits and crackers. Enzymes used include amylases, hemicellulases, amyloglucosidase, protease. Amylases and hemicellulases are applied to improve and standardise the quality of the bread (e.g. softness, volume, crumb quality). Amyloglucosidase is used to ensure an even browning of the crust. Proteases are applied to decrease the level of protein in flours for biscuits/crackers.

Beverage industry: In fruit juice manufacturing mostly pectinases are used to increase the juice yield (decrease the amount of waste) and to improve the quality (clarification, removal of pectins). Pectinases and other enzymes are also involved in the wine-making process to help maintain colour, clarity and organoleptic properties. The brewing process involves enzymes in order to break down the polysaccharides in the starting cereals to fermentable sugars. Microbial enzymes can be used to control the brewing process more precisely by compensating for differences in the quality (enzyme content) of the malt. Other enzymes (e.g. fl-glucanase) are used to prevent chill-haze (the beer becoming cloudy upon cooling).

Dairy Products:
For the making of cheese the enzyme chymosin is used. Other areas where enzymes find application are in the improvement of organoleptic qualities of some cheese and to break down lactose (milk sugar) in order to make dairy products digestible for people with lactose intolerance.

Starch and Sugar:
Amyloglucosidase and glucose isomerase are widely used in the hydrolysis of starch to glucose and in the conversion of glucose to fructose. Fructose the naturally occurring sweetener in honey and fruits, is 40% sweeter than sugar but has about the same calorific value and is thus widely used as a sweetener.

Animal feed industry
For the animal feed industry, adding feed enzymes to feed stuff represent a means of improving feed utilisation and reducing pollution from excretory products. Feed enzymes are degrading specific feed components which are otherwise harmful or of little or no value. In doing so, a wider range of ingredients may be used in diet formulation. Feed enzymes may be used to increase the amount of nutrients available from vegetable proteins or to substitute a previously unacceptable energy source for another (e. g. barley for wheat in broilers). A further benefit lies in the reduction in faecal nutrient level, which may be important where faeces are applied to land with restrictions. Feed enzymes in combination with endogenous enzymes degrade compounds so that they can be utilised by the animal.

Modified starches

Starch is made up of a mixture of the two polysaccharides amylose and amylopectin. Both amylose and amylopectin consist of large amounts of glucose units, which are joined together by glycosidic bonds (Abbas et al., 2010). Starch is produced by all green plants as a source of stored energy for the plant. Globally, starch is primarily produced from maize, however is also found in all cereals, potatoes, and rice (Abbas et al., 2010; Singh et al., 2010). Starch in its raw form (i.e unmodified) is not extensively used in the food industry due to the production of weak-bodied, cohesive, rubbery pastes when heated and undesirable gels when the pastes are cooled (Abbas et al., 2010).

Starch can be modified by physical or chemical treatments which results in changes in gel strength, flow properties, colour and stability of the paste (van Dongen et al., 2008). Abbas et al. (2010) has reported a number of uses of modifed starches in the food industry these include use as a fat replacer in low fat foods (i.e maltodextrin), as a texture improver in bread making and battered products and as a method to ensure even browning and crispiness of fried snack products.

Modified starches can be used as a functional food in health food products as the resistant starch can be considered to be a third form of dietary fibre. This resistant starch can be added to breads and cookies to develop high fibre products for use as a healthier alternative to existing products available. Singh et al. (2010) has reported that modified starches can be used during the canning process to thicken, stabilize and enhance the texture of canned foods such as puddings, fillings for pies, soups, sauces and gravies. During the production of frozen food products modified starches are used to provide freeze–thaw stability and retro gradation.

Modified starches can be used in non–food applications such as in the pharmaceutical industry and as a thermoplastic starch biopolymer (thermoplastic starches are discussed in a separate section of this report).

In the pharmaceutical industry modified starches can be used as conventional excipients. It can also be used as a superdieintegrant when the active ingredient needs to be made available in a short period of time, such as in fast acting pain relief tablets (Singh et al., 2010). Starch which has been modified with ethylene oxide produces hydroxyethyl starch, this is mainly used as plasma volume expander, which is useful for the patients suffering from trauma, heavy blood loss and as cancer treatments (Singh et al., 2010). Andreev (2004) reported the disintegration time of a-lactose monohydrate tablets containing 4% of sodium glycolate starch made from potato starch to be approximately 10 seconds compared to 40 seconds for wheat starch, 50 seconds for maize starch and 140 seconds for rice starch.

The production of modified starches in Ireland should fit well with the presence of large international food ingrident producers such as Kerry and the large pharmaceutical industry present in the country.

Amino Acids & Vitamins

Amino acids are the building blocks of protein which is required to sustain life. Most amino acids are produced by living animals. Amino acids which are not produced by the body are called essential amino acids and must be supplied through feed. These essential amino acids include lysine, methonine and threonine which are present in only small amounts in plant material (Kircher & Pfefferle, 2001). The low amounts of lysine present requires the addition of high lysine soybeans or pure lysine to feedstuffs (Zika et al., 2007). Animals need to consume feedstuffs until the limiting amino acid is met. However, the amino acids readily present in the feedstuffs cannot be converted into protein and is excreted from the animal resulting in high N emissions (Kircher & Pfefferle, 2001).

The production of lysine can be conducted by fermenting glucose with a strain of *Corynebacterium glutamicum*. Addition of lysine to feedstuffs for animals would result in lower amounts of feed being required with no loss of weight gain. The better utilization of feed also reduces emissions of N and has a positive impact on the economics of meat production. Zika et al. (2007) estimates the global market for lysine stands at €1.2 billion, at a price of €1.20 kg^{-1}. Based on feed consumption data, Western Europe requires 268,000 t of lysine year^{-1}. Current production levels of lysine in Europe stand at 130,000t year^{-1} (Zika et al., 2007). Other amino acids currently being produced by fermentation methods include methionine and threonine. Table 3 shows the global production of amino acids for the year 2007 with the market sizes of each amino acid included. From this it can be seen that L–Glutamic acid also known as MSG, L–Lysine–HCL and DL–Methionine have a combined market value of $5.3 billion and a combined tonnage of 2.58 million tonnes.

Table 3: Global production of amino acids and market values, adapted from (Demain, 2007).

Amino Acid	Process[a]	Tonnes Year^{-1}	Market ($)	Titer (g L^{-1})
L–Alanine	E	450	–	75
L–Arginine	F	1,000	150 million	96
L–Aspartic acid	E	9,000	43 million	–
L–Cysteiine	E	2,700	4.6 million	–
L–Glutamic acid	F	1,450,000	1.5 billion	85
L–Glutamine	F	1,200	–	–
Glycine	C	20,000	–	–
L–Histidine	F	360	–	42
L–Isoleucine	F	360	–	40
L–Leucine	F	450	–	34
L–Lysine–HCL	F	770,000	1.5 billion	170
DL–Methionine	C	360,000	2.3 billion	–

L–Phenylalanine	F	11,500	198 million	51
L–Proline	F	320	–	100
L–Serine	F	270	–	65
L–Threonine	F	63,500	270 million	100
L–Tryptophan	E	2,700	150 million	58
L–Tyrosine	F	150	50 million	26
L–Valine	F	450	–	99
Total	–	2,700,000	6.17 billion	–

[a] E; Enzymatic process, F; Fermentation process, C; Chemical synthesis process.

Vitamins that can be produced by microbial and fungal fermentation include vitamin B_2, ribose and vitamin B_{12}. Vitamins are defined as essential micronutrients that are not synthesized by mammals (Survase et al., 2006).

Riboflavin (Vitamin B_2) is used for human nutrition and therapy and the crude concentrated form is used as an animal feed additive. Current global production of riboflavin is in excess of 4,000 t year^{-1}, of which approximately 25% is used for food and pharmaceutical purposes and the remaining 75% used as an animal feed additive. The two, closely related, main fungi used for the industrial production of riboflavin are *Eremothecium ashbyii* and *Ashbya gossypii* (Shimizu, 2008). Table 4 shows the global production of vitamins from the year 2007. The largest markets for vitamin production from biological processes include Pantothenate, Vitamin C, B_{12} and B_2, with a combined value of $881 million.

Table 4: Global production of Vitamins and market values, adapted from (Demain, 2007).

Vitamin	Process[a]	Tonnes Year^{-1}	Market ($)
Biotin	C	80	64 million
Provitamin A	C, E, F	90	–
Folic acid	C	480	17 million
γ–Linoleic acid	F	900	–
Niacin	C	25,000	133 million
Vitamin B_{13}	F	90	–
Pantothenate	C, F	9,000	156 million
Provitamin D3	C, E	450	–
Vitamin B_6	C	3,500	70 million
Riboflavin (B_2)	F	4,200	134 million
Thiamine (B_1)	C, F	3,400	67 million
Tocopherol	C, E	9,000	–
Vitamin A	C	2,500	308 million
Vitamin B_{12}	F	23	105 million
Vitamin C	C, B	97,000	486 million
Vitamin E	C, E	27,000	89 million
Vitamin F	E, F	900	–
Vitamin K_2	C	1.8	–
Total	–	183,615	1.63 billion

[a] C; Chemical synthesis process, E; Extraction Process, F; Fermentation process, B; Bioconversion process.

Discussion

A number of high value products can be developed from crop options. The high value products are primarily derived from either fermentation or enzymatic conversion of sugar and starch portions of a crop. The main crop options for these feedstocks would include sugar beet and potatoes grown primarily for starch production.

Ireland's economy (excluding agriculture) is primarily based around highly specialised and focused products including pharmaceuticals and computer components. There is no significant heavy industry present in Ireland. The production of commodity chemicals for use in heavy industries from bio–based methods would not sit well within an Irish context. Also due to the relatively small amount of tillage land available within Ireland the production of commodity chemicals may not be cost effective. The production of lower volume higher value products such as antibiotics, pharmaceutical products and amino acids may be a more economically sound investment.

The production of biopolymers that are suitable for use in the pharmaceutical and computing industry would allow for residual feedstocks to be utilised increasing the economic returns to farmers. To achieve cost effective levels of fermentative product production an integrated bio–refinery would need to be constructed. This facility would combine a number of companies who would construct the plant together. This would allow for the full feedstock to be used and synergies to be developed both increasing the profitability and environmental benefits of the facility. Development of the bio–refinery as a form of co–op facility would allow for best returns to farmers and allow for strong growth of the market, similar to that seen in the dairy industry.

Conclusions

Development of high value products, which are fermented from glucose, can be produced in Ireland. The production of these products would likely require a re–introduction of sugar beet into Irish agriculture and the construction of a bio–refinery. High value, specialised, products should be focused on instead of commodity chemicals and polymers. With large pharmaceutical and food ingredient companies already present in Ireland, we have an advantage over other European countries for the production of these speciality products.

The products presented in this report all require the establishment of processing facilities (i.e. an integrated bio–refinery) and are therefore suitable for consideration as crops to farmers in the medium to long term.

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