Hydrophobic Polymers from Food Waste: Resources and Synthesis

S. A. Sanchez-Vazquez [a] , H. C. Hailes [a] & J. R. G. Evans [a]

[a] Department of Chemistry , University College London , London , England, UK
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S. A. SANCHEZ-VAZQUEZ, H. C. HAILES,
AND J. R. G. EVANS

Department of Chemistry, University College London, London, England, UK

The food waste generated annually is approximately 1.3 Pg. It contains chemical feedstock that could be diverted to materials production as the mineral oil price rises, incurring no conflict over land use and providing new wealth-creating opportunities for food-producing countries. It potentially realigns the industrial and agricultural sectors of national economies. Food waste production scales with population as does demand for materials. This review builds upon previous landmark papers in Polymer Reviews that address biomass in polymer production. It surveys the current global food-waste resource and demonstrates how it could be used in the generation of hydrophobic polymers.

1. Introduction

1.1 Economic Context

In setting out the context for sustainable materials it is important to establish the motivational factors, controversial and uncertain as they are at present. It is not universally accepted that substitutes for fossil fuels are needed because they are "running out": the economic situation is less dramatic and the transition is likely to be quite smooth. The upper bound for stored carbon is set by the high CO_2 content of the second atmosphere from which carbon was fixed by life forms into limestone and buried carbon. Estimates of these distributions, based partly on the isotopic distribution of ^{13}C and ^{12}C between marine sediments and photosynthesized biomass, respectively,[1] indicate that the reservoir of carbonate is 60 Zg and that carbon in rock is present at 15 Zg.[2] One of the best assessments of oil reserve data from a disinterested perspective is provided by Vacal Smil of the University of Manitoba.[3] There is a long history of claims that peak oil production has passed, each of which is followed by new resource discoveries. Smil suggested that the estimated ultimate recovery is about 3 Tb but his publication preceded several large discoveries, notably the Bakken Formation announcement in

Address correspondence to J. R. G. Evans, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England, UK; E-mail: j.r.g.evans@ucl.ac.uk
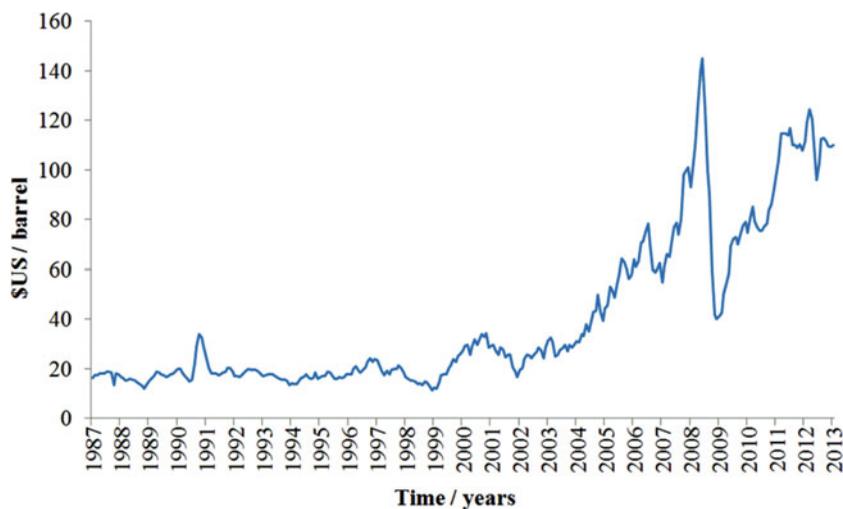
Figure 1. Twenty six year oil price (Brent Crude spot price): the upward trend invites new business from biomass processors but the instability inhibits such investment.[11] Compiled from data published by the International Energy Agency (Color figure available online).

2008. The USGS report[4] shows that the Bakken holds $6 \times 10^8 \, m^3$ of technically recoverable oil alone ($\sim$26 EJ). Globally, proven reserves (1P) are about 1.3×10^{12} barrels (2.1×10^{11} m^3 or 8 ZJ). Reserves of the three fossil fuels are 31 ZJ with oil and gas making up 40%.[5] An optimistic assessment of the European oil and gas supply futures has also been made by Aguilera[6] and the indications are that shortages of fossil fuels are not imminent.

The wider picture is that as the oil price increases (Fig. 1) due to novel extraction techniques, new technologies such as coal-to-liquid, gas-to-liquid, and methane hydrate extraction will become economically viable, that is, the expected price level minus the costs of development and production leave a profit acceptable to the producer. For this reason, the liberation of fossil carbon into the atmosphere is unlikely to be arrested by resource depletion. The huge investment by China in coal to liquid fuel conversion[7] has been temporarily curtailed but similar technologies mean that there is likely to be no shortage of coal-sourced, synthetic liquid fuels. Although many reserves of coal, oil, clathrates, or gas are not economically recoverable at present, technical and market circumstances have been changing. The extraction of methane from clathrates, for example, is beginning to be assessed.[8] Increase in the oil price (Fig. 1) stimulates both vigorous exploration and new extraction technologies but also entirely new fossil carbon fuel sources. Each of these presents a "learning" or "experience" curve in the form of a logarithmic decrease in price with time and output.[9] The importance of the learning curve in determining investment decisions in alternative energy technologies is emphasized in a University of Melbourne report[10] which explores the decreasing costs of photovoltaic, wind and solar concentrating energy collection as a function of deployment.

A rise in oil price also provides a market stimulus for biomass sourced fuels such as bioethanol and biodiesel and for chemicals and polymer production, each associated with its own learning curve. This offers a prospect of sustainability in materials. The free market, responding to a combination of oil price rises and the evolution of regulatory measures to address climate change may therefore encourage the materials industries to use the biomass resource.

The short term motivational factor in seeking independence from fossil fuels is based on political instability and political interference in the free market. A UK Government report[12] sets out these perceived threats and a 2010 report defines the emergency responses in terms of International Energy Agency (IEA) policy on stockpiling;[13] but this is a short term measure. The wider and longer term issue is climate change associated with the steady increase of atmospheric carbon dioxide which is at present closely linked to economic activity. The feedback effects of warming include loss of polar albedo and liberation of methane from the melting of frozen soils.[14–16] The global effects on health have been clearly defined[17] and the security issues anticipated[18] so that there is a strong societal motivation to launch now those remediation technologies which have a long technical lead-time. The commercial motivation in the context of lead-time is more complex as discussed below.

The polymer materials community has responded to environmental issues in several ways, notably through recycling schemes and the introduction of biodegradable packaging but perhaps the greatest response is the growth of interest in a materials science and technology that uses "no new carbon" and therefore makes use of biomass in order to preserve economic growth.[19] In the last decade there has been renewed and growing interest in biomass-sourced hydrophilic polymers, particularly as reinforcing fibers in polymer composites where they can deliver a 2:1 modulus mismatch,[20–23] but also as bulk polymers in their own right. Moreover, the various routes to the synthesis of hydrophobic polymers are being explored and extended and several reviews have appeared that address both classes of polymer.[24–27] These ideas are not new. In 1940, Henry Ford patented a car body shell made from a soybean-based polymer supported on a tubular steel frame.[28] It saved one third of the weight of a steel body and Ford believed it was safer. Ford had a complex relationship with his farming roots and saw the car as a way to combine industrial and agricultural enterprises. This aspect of Ford's vision is by no means irrelevant today. The sectorization of economies, particularly between industry and agriculture is reflected in the relative wealth of nations with agriculturally-based economies tending to be poorer and the prospect for biomass-sourced polymers represents a "synthesis" in more ways than one and a paradigm for the emerging idea of "integrated" or "balanced sector economics."

Carbon emissions trading tends to favor the developed nations because the baseline is set by current emissions and it seems increasingly likely that large trading blocks that have been active in emissions control will be prompted to enforce policy on others through climate change trading regulations such as import taxation on embedded fossil carbon. This might be set at levels that are informed by available technology so that if it is possible, within a trading block, to build a car with a carbon output of 50 g/km, the import tariff threshold might be set at 100 g/ km. Similar restrictions would apply to the import of materials, again informed by what is possible in large scale production operations. Research in biomass materials is therefore both a preparation for tomorrow's markets and an influence on the regulations that will shape them. It seems that competition between manufacturers, in the context of climate change, is going to become partly about regulation setting.

Here we focus on synthetic pathways to engineering polymers that begin with industrial food waste. These starting materials avoid the conflict of land use between food crops and raw material crops that has been problematic in the development of biofuels.[29,30] The prospective increase in reliance on biomass is controversial: Patzek argues forcefully[31] that a one-to-one replacement is impossible but the local situation is more complex; regions of sub-Saharan Africa and China for example have land areas that could be deployed for agriculture, which can be viewed as a form of solar energy harvesting, particularly in the context of crops bred or modified for enhanced survival. Changes to oil price and to

environmental regulations may therefore conspire together to change the role of agriculture in supplying food, materials, and fuel.

The enterprises that benefit from these new markets will be those which have done the preparative work and shortened their technical lead-time with respect to their competitors once the market summons them. As such, the lead time of a product matters not for its own sake, but because once a rival firm begins the process of working towards production or reducing its own lead times it takes the competitive advantage. It is for this reason that a firm is only likely to be motivated to begin work on a new technology where it believes that technology will deliver sufficient profit and where it believes current lead times must reduce in order to remain competitive and in some cases gain first mover advantage. In this instance, first mover advantage is likely to be enjoyed by the firm with the technological leadership to capture the emerging market first and may therefore enjoy high profit margins and monopoly-like status. Already a significant number of companies have established a foothold in this market and are developing their expertise based on long term market assessments.[32] The properties of biopolymers presently on the market are summarized by Endres.[33] Nova-Institute GmbH and Bioplastics Magazine have published the 2012/2013 International Business Directory for innovative bio-based plastics and composites in which they list the major suppliers of biopolymers in the world.[34] These surveys indicate that the market is beginning to summon biomass resources for polymer production.

It is against this quite complex and uncertain motivational background that we first explore the main sources of available food waste stock, identify the useful raw materials that can be extracted and then discuss the various polymerization routes that can be identified.

1.2 Definitions

The term "biopolymer" generally refers to polymers that have been fully synthesized by living organisms and there are three main subsets: polysaccharides, polynucleotides and polypeptides. Indeed, ASTM D6866 defines biopolymers as polymers produced by living organisms, that is, polymers synthesized in nature by enzyme-catalyzed chain growth polymerization reactions by complex metabolic processes in the cells of organism during their growth cycles.[35] They are also referred to as natural polymers. A somewhat more general definition includes three categories: (i) those extracted directly from raw materials, (ii) those produced by chemical synthesis from bio-derived monomers or precursors and (iii) those produced by microorganisms or genetically modified bacteria.

This extension to the definition muddies the water and leads to confusion in the meaning of "biopolymer." The three meanings are distinct from the synthesis/processing viewpoint although from the economic and environmental viewpoint they may be indistinguishable. In some cases, the end product might be indistinguishable from that derived from mineral oil except by isotopic assay: the dehydration of bio-ethanol as a source for polyethylene is an example.[36] The emphasis of this review is on polymers that are synthesized from feedstocks that derive from biomass rather than from mineral oil and most therefore fall into the second of these definitions, more specifically we address the category of biomass-sourced hydrophobic polymers although these are necessarily placed in the context of other biomass-sourced polymers.

When used as materials, particularly as structural materials, biopolymers are sometimes referred to as bioplastics. Most bioplastics are degradable and some can be composted such that they are both renewable and biodegradable making them sustainable materials. The term bioplastic is therefore unsuitable for hydrophobic polymers derived from biomass that are intended for long term structural applications resisting photo- and bio-degradation.

The term agro-polymer meaning a renewable and compostable polymer derived from plants is almost a synonym for biopolymer. In contrast the term biomaterial is normally used in a medical context with quite a different meaning: "any material that is used in conjunction with living tissue to augment repair for example as a prosthetic device or in wound management." Some biopolymers can be used as biomaterials because of their steady decomposition in-vivo to non-toxic products.

A bio-based product is a material derived in whole or in part from biomass resources. Two methods to measure the bio-based content of a material are specified in the ASTM D6866 standard which measures the $^{14}C/^{12}C$ ratio to determining the amount of carbon in products derived from contemporary as opposed to fossil sources.

There is increasing interest in the production of environmentally benign composites designated biocomposites or green composites from biopolymeric matrices and natural fibers which provide alternatives for oil-sourced polymers and glass or carbon fibers, respectively. An example is the development of a composite of poly(lactic acid) (PLA) and agricultural by-products which contains a high quantity of cellulose-based fibers such as wheat straw, soy stalk, and corn stover.[37] As agricultural residues are from 8 to 10 times cheaper than agricultural fibers, the goal is to create cheap sustainable injection molded composites with superior properties such as low density, renewability, and biodegradability.

The term white technology, or white biotechnology, is an alternative for industrial biotechnology and refers to the use of biotechnology in the chemical industry for the production of fuels or materials employing, inter alia, cells and enzymes.

1.3 Biogenesis Considerations

The available quantities of compounds derived from food waste can be assessed by classification of metabolites. In the traditional classification, primary metabolites are small molecules essential for the development, growth, and reproduction of an organism that are formed by catabolism-degradation pathways and anabolism-synthesis pathways. These metabolic pathways are common across all organisms. Primary metabolites include sugars, amino acids, nucleotides, acyl lipids, and "simple" fatty acids. They are relatively few in number and have a wide distribution across many species.

Other metabolic pathways exist that generate secondary metabolites that on initial inspection appear to have no essential utility. They are formed via secondary metabolism pathways that may be switched on by certain stimuli such as defence, attraction, and ultraviolet protection, enabling, for example, a specie to establish an ecological niche with a plant defence compound or attractant. Many secondary metabolites currently have unknown function. They are extremely diverse in structure, tend to be classified by biosynthetic origin and are invariably found in small quantities in a limited number of species within a phylogenetic group. They are broadly classified into alkaloids, terpenes, glycosides, phenols, polyketides and fatty acid derived products, and non-ribosomal peptides. Larger molecules include DNA, RNA, biopolymers, and proteins are often excluded from the classification.

The line between primary and secondary metabolites is not clear cut, for example, some steroids that have an essential structural role can be classed as primary metabolites. Also, the biopolymer lignin is the second most abundant organic material in plants. Although it is essential for structural purposes, it is considered not as a primary metabolite but a secondary metabolite. Primary metabolites are considered to be involved in the essential metabolic processes for basic cell metabolism, while secondary metabolites affect the interaction between organisms and the environment. The metabolisms are closely related as primary

metabolites are frequently the starting materials for secondary metabolite production, such as amino acids for alkaloid production, acetates for polyketide and terpene synthesis, and shikimate for the synthesis of aromatics. The widely used categorization of compounds into the broad primary and secondary metabolite groups has recently been revisited because too many important chemicals do not fit into either of these two groups, such as carotenoids and some lipids.[38]

Within the primary and secondary metabolites, there is wide diversity of chemical types with similar physicochemical characteristics. Chemists and materials scientists who are accustomed to the extensive heterogeneity of the mineral stock, on first approaching the biomass resource are justified in asking: Given the huge diversity of species, why are there so few high yield primary metabolite types? The classification of metabolites into primary and secondary first proposed by Kössel is also questioned partly because of its lack of evolutionary base and lack of insight into metabolism.[38] In evolutionary terms, the primary metabolic pathways were established at an early stage and it became harder to improve upon them; evolutionary convergence may have strengthened the canalization. It is argued, therefore, that the derived properties of biomolecular activity and physicochemical behavior of primary metabolites provides an alternative classification under "basic integrated metabolism" together with "supported metabolism."

In general, the primary metabolites that are obtained commercially are high volume-low value bulk chemicals such as simple fatty acids. Secondary metabolites, however, since they are found in smaller quantities, can be difficult to isolate and exhibit a range of bioactivities have a higher commercial value and find applications as fine chemicals and pharmaceuticals. Examples include morphine, cocaine, quinine, and limonene. Structurally many possess multiple chiral centres and rings and are difficult to synthesize chemically at low cost.

2. A Survey of the Sources, Amounts, and Constitution of Food Wastes

Food waste totals 1.3 Pg annually.[39] As the technology of food-processing develops, the pre-consumer food loses tend to decrease but in the developed countries, consumer food waste tends to be greater. At present many of these wastes are uneconomically used and are often disposed of in the local environment, causing pollution issues.

The agro-industrial wastes that are available in large amounts include among others, citrus skin and pulp (orange, grapefruit, mandarin/tangerine, lemon, lime), seed waste (mango, grape, pumpkin), skin (potato and banana), peanut husk, coffee, sugar bagasse, and straw. These wastes contain high contents of organic matter and, as seen in Tables 1 and 2, they are rich in ash, fat, fiber, protein, and carbohydrates that can be used in several secondary applications. There is a global research effort to investigate new profitable uses.

The most common current uses are as inexpensive cattle feed or crop fertilizer but other applications make use of food wastes as renewable sources of pectins, natural fibers, oils, and as a culture medium for fungi. They are also used for the production of renewable energy from combustion or as methane and biogas or biofuel sources. The food waste biomass resource could be categorized by the major available component but this taxonomy leads to confusion because it is often the lower yield products that have value and can be sourced from many species across different categories. Similarly a classification based on highest current usage of biomass products can quickly become outdated. For these reasons we first consider the main food waste resources individually, examining their constitution, availability and current uses. This makes it easier to explore the resources which could be used to develop new markets in hydrophobic polymers.

Table 1

Substances found in the industrial food wastes

| | Peanut Husk[40] wt.% DM | Potato[41,42] wt.% DM | Mango seed[43] wt.% | Sugar Bagasse[44] wt.% DM | Citrus peel[45–47] | | | | |
					Grapefruit wt.%	Lemons wt.%	Lime wt.%	Orange wt.% DM	Mandarin wt.% DM
Moisture			40.5		8.2	10.6	10.1		
Protein	7.39	10.2	1.43	0.5	4.9	9.3	9.7	9.1 ± 0.4	7.5 ± 0.2
Fatty acids		0.40	4.92					4.0 ± 0.2	1.6 ± 0.1
Fiber	26.2	2.40	3.96		11.9	14.9	14.4		
Lignin				24.8				7.5 ± 0.6	8.6 ± 0.8
Cellulose	22.5		48.19		27.8			37.1 ± 3.1	22.6 ± 2.2
Lipids		0.06							
Hemicellulose	18.33							11.0 ± 1.1	6.0 ± 0.6
Starch		67.5							
Sugar		0.7						9.6 ± 0.2	10.1 ± 0.5
Pectin				0.7				23.0 ± 2.1	16.0 ± 1.2
Ash	7.79			3.9	4.2	5.2	5.1	2.6 ± 0.1	5.1 ± 0.2
EE[a]	6.31		0.83		1.1	2.8	2.9		
FNE[b]	52.4				69.6	67.8	67.9		

[a]EE = Ether extract is the method used to determine the content of lipids (fat and oil) in feedstuffs.[48]

[b]Nitrogen free extract (NFE) is an estimate of soluble carbohydrates like crude starch and sugar content of a feed. This content is not analytically determined, but is calculated by difference with the equation: % NFE = % Dry Matter − (% Ether extracts (Fatty acids) +% Crude protein +% Ash +% Crude Fiber), the estimation of NFE accumulates all the errors that exist in the analysis of the other components.[48,49]

Table 2

Substances found in the industrial food wastes

| | Coffee[50] | | Avocado seed[51] | Wheat straw[52] | Banana peel[53] | Corn stover[54] | Carrot[55–57] | | |
	Pulp wt.% DM	Husk wt.% DM	wt.%	wt.% DM	wt.% DM	wt.% DM	Pomace wt.% DM	Peel wt.% DM	Leaf wt.%
Moisture			56.0 ± 2.6						7.2 ± 0.1
Protein	10	9.2	2.0 ± 0.2	7.8 ± 2.2	7.9		8.4 ± 0.2	9.7 ± 0.3	15.2 ± 0.5
Fatty acids	2.5	2			11.6				
Fiber	18		5.1 ± 1.1	54.6 ± 0.61	7.7		63.5 ± 1.5	45.5 ± 0.4	12.0 ± 0.3
Lignin				4.2 ± 1.3		11.0 ± 1.8			
Carbohydrates[a]	50	57.8	33.2 ± 2.7		59.5	27.8 ± 2.8	19.3	33.0 ± 0.8	52.7 ± 0.7
Cellulose				28.0 ± 0.59					
Lipids			1.9 ± 0.3				1.1 ± 0.1	1.5 ± 0.1	
Hemicellulose				22.3 ± 0.76		32.0 ± 2.6			
Starch									
Sugar									
Pectin		12.4				7.8 ± 1.6			
Ash			1.9 ± 0.2		13.4		7.7 ± 0.01	10.3 ± 0.3	10.5 ± 0.3
FNE[b]									2.5 ± 0.1

[a]The data for carbohydrates is not subdivided.

[b]Nitrogen free extract (NFE) is an estimate of soluble carbohydrates like crude starch and sugar content of a feed. This content is not analytically determined, but is calculated by difference with the equation: % NFE = % Dry Matter − (% Ether extracts (Fatty acids) + % Crude protein + % Ash + % Crude Fiber), the estimation of NFE accumulates all the errors that exist in the analysis of the other components.[48,49]

This survey of the food waste resource indicates the raw materials that are potentially available, *inter alia*, for the production of biopolymers. Where the total amount of waste is indicated, this is calculated from the total worldwide production which is not the same as the industrial food waste.[58] It is the industrial waste that is collectable as agricultural, postharvest, processing, and distribution wastes and is sufficiently uncontaminated that it can be used in secondary processes such as polymer production. Some authors[39] use the term "food losses" to describe pre-consumer waste thus reserving the term "waste" with its attendant value-judgement for domestic or consumer waste. The proportions of industrial and consumer waste vary with food type.[39] For example, 16% of initial production of cereals is pre-consumer loss and a further 12% is lost by the consumer on average. These proportions vary geographically, the more affluent nations tending to have higher consumer loss and lower pre-consumer losses. For roots and tubers, on the other hand, the pre-consumer loss is 40% of initial production and consumer loss only 6% on average. For oilseeds and tubers pre-consumer losses again dominate at 20% while the consumer loses only 2% on the initial production. In can generally be assumed that consumer wastes are too contaminated for secondary processes other than gasification.

2.1 Potato Waste

Potato (*Solanum tuberosum L.)* is particularly popular in Europe:[59] the UK per capita consumption was 102 kg in 2005. Approximately 25% of the input to a potato processing plant emerges as waste, consisting of a portion of the peel and whole or cut potatoes discarded due to size, blemishes, or failure to meet quality standards.

China is now the biggest potato producer at 72 Tg per year (Table 3) and almost a third of all potatoes are harvested in China and Russia. Starch is the main resource at 68% based on dry weight (Table 1) and uses for starch in polymers and as a precursor to furan derivatives is described in section 3.1.1.

Potato waste is also a source of polyphenols which are found mainly in the subsurface. The structures of polyphenols and chlorogenic acid isomers found in the potato tuber are shown in Table 4. Chlorogenic acid constitutes 90% of the total phenolic content. The possible polymerization of these minor constituents is discussed below.

Table 3
Production of potato (data for 2007)[59]

Country	Production/Tg
China	72
Russian Federation	37
India	26
USA	20
Ukraine	19
Poland	12
Germany	12
Belarus	9
Netherlands	7
France	6
World	325

Table 4
Structures of potato polyphenols and chlorogenic acid isomers[60]

Structure	Common name	Synonym	IUPAC nomenclature
$R^1=R^2=R^3=R^4=H$	cinnamic acid	—	(E)-3-phenylprop-2-enoic acid
$R^1=OH$, $R^2=R^3=R^4=H$	p-coumaric acid	4-hydroxycinnamic acid	(E)-3-(4-hydroxyphenyl)prop-2-enoic acid
$R^1=R^2=OH$, $R^3=R^4=H$	caffeic acid	3,4-dihydroxy-trans-cinnamic acid	(E)-3-(3,4-dihydroxyphenyl)prop-2-enoic acid
$R^1=OH$, $R^2=OCH_3$, $R^3=R^4=H$	ferulic acid	4-hydroxy-3-methoxycinnamic acid	(E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid
$R^1=R^2=OH$, $R^3=$quinic acid $R^4=H$	chlorogenic acid	3R-[[3-(3,4- dihydroxyphenyl)-1-oxo-2-propenyl]oxy]-1S,4R,5R-trihydroxy-cyclohexanecarboxylic acid	(1R,3R,4S,5R)-3-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,4,5-trihydroxy-cyclohexane-1-carboxylic acid
$R^1=OH$, $R^2=R^4=OCH_3$, $R^3=H$	sinapic acid	4-Hydroxy-3,5-dimethoxycinnamic acid	(E)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid

Table 5
World's corn production 2009[51]

Country	Production/Tg
USA	333.0
China	164.1
Brazil	51.2
Mexico	20.1
Indonesia	17.6
India	16.7
France	15.3
Argentina	13.1
South Africa	12.1
Ukraine	10.5
World	818.8

Large amounts of potato waste are left in open fields to decompose and some used to feed cattle which can consume up to 12% of their body weight of fresh potatoes daily: potato delivers four times the energy value of cereal grain for beef cattle.[41] Several novel projects have addressed the opportunities provided by the extensive availability of potato waste. In one example, potato waste, digested in four stages—hydrolysis, acidification, acetogenesis, and methanogenesis enabled a biogas plant to provide electricity to the public grid and to preheat industrial dryers.[61] This technology has also been applied in the UK.[62] Another application is the use of potato waste as a new medium for the fermentation of xanthan,[63] a thickening agent used in food products and currently obtained expensively from sugar. Polylactic acid (PLA) has also been produced from potato waste which can be used as a non-petroleum based polymer.[64]

2.2 Corn Stover

Corn, also known as maize, has been a dietary staple in the Americas since prehistoric times. According to the Food and Agriculture Organization of the United Nations (FAO),[51] in 2009, 819 Tg of corn were harvested and the USA produced 333 Tg per year, 40% of the world's total production. Ten countries who contribute 70% of worldwide production are listed in Table 5.

Corn waste (or corn stover) compromises five parts: nodes, leaves, shell, core, and sheath; the morphological structure is shown in Fig. 2. At harvest, the grain represents only 15% of the weight; the rest is treated as food waste. This means that around 696 Tg of total corn waste is produced each year.

The components of corn stover are shown in Table 6. This is the most abundant lingo-cellulose renewable resource in the world due to its chemical composition and the enormous quantity produced annually worldwide. As seen in Table 6, 70% of the total corn stover is composed of ligno-cellulose corresponding to 487 Tg.

The main application for corn stovers is as fertilizer but new opportunities for its use are emerging, among them research on enzymatic hydrolysis and solid state fermentation [54] and as a renewable source for ethanol production[66] using *Pichia stipitis*,[67] a cellulolytic ex-tremophile[68] or with biocatalysts.[69] Another application is in the production of biopolymers.
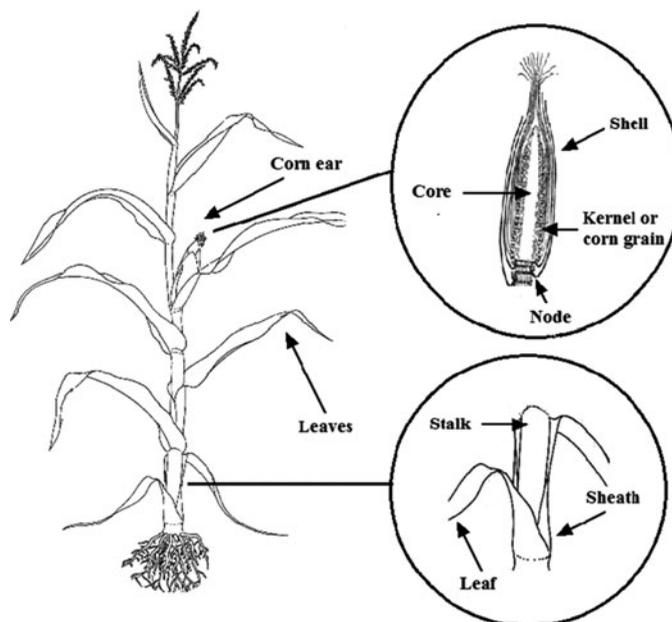
Figure 2. Corn stover structure.

Polyhydroxyalkanoates (PHA) can be produced from corn grains but there are attempts to produce it in combination with corn stover.[70]

Another approach is the chemical liquefaction of the lignocellulosic materials in the corn stover, which is about 71% (Table 6) of its total composition, using ethylene carbonate and/or ethylene glycol as solvent and sulphuric acid as catalyst for the preparation of polyols. The lignocellulosic material is partially degraded into polyols, providing OH groups which can be used for the production of polymers without further separation, modification, or purification. Biodegradable polyesters can be obtained by cross-linking the polyols with multi-functional carboxyl acids and/or cyclic acid anhydrides.[71] Furthermore, the polyols obtained can be used directly for the preparation of polyurethane foams by a one-shot method using dibutyltin dilaurate as co-catalyst, silicone as surfactant, and water as blowing agent. The mechanical strength of the polyurethane foams obtained can be controlled and

Table 6
Chemical composition of corn stover[54]

Part	Weight ratio (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Acid insolvable ash (%)
Leaf	32.0	26.2 ± 2.3	33.9 ± 1.9	9.3 ± 1.4	11.6 ± 1.5	1.6 ± 0.6
Shell	9.4	36.7 ± 3.2	27.5 ± 2.2	14.2 ± 1.0	4.6 ± 0.2	0.5 ± 0.2
Core	15.4	33.3 ± 4.9	32.2 ± 3.2	10.1 ± 1.8	4.9 ± 1.1	0.5 ± 0.2
Node	22.9	28.9 ± 3.9	32.2 ± 2.4	12.5 ± 1.5	5.4 ± 1.3	0.5 ± 0.1
Whole	100	27.8 ± 2.8	32.0 ± 2.6	11.0 ± 1.8	7.8 ± 1.6	0.9 ± 0.3

Table 7
World production of mango (2008 data)[51]

Country	Production/Tg
India	13.6
China	4.0
Thailand	2.4
Indonesia	2.0
Mexico	1.9
Pakistan	1.8
Brazil	1.2
Bangladesh	0.8
World	34.9

improved by using polymethylene polyphenylisocyanate (PAPI) as co-monomer which varies the [NCO]/[OH] ratio in the structure of the foam.[72]

2.3 Mango Seed

Mango (*Mangifera indica*) is a native tropical fruit from southern Asia which is now cultivated in most frost-free tropical and warmer subtropical climates. Seven countries are responsible for almost 74% of the entire world production of mango (2008 data).[51] India is the largest producer with 13.6 Tg equivalent to 39% of world production (Table 7). During the processing of mango, peel and almond are generated as waste materials and they represent around 40-50% of the total fruit weight so that the total world production yields approximately 15.7 Tg of mango waste per annum.

The mango almond contains high quantities of carbohydrates (such as starch), fat, and fiber (Table 8). Through microbial fermentation it is possible to obtain pectins, comestible fibers, vinegar, and citric acid.[73]

The almond contains around 5% of fat, 95% composed of neutral lipids, and the reminder of polar lipids. The oil obtained consists of 44-48% saturated fatty acids and 52-56% unsaturated.[43] Oleic acid is the primary component at 40.8% and protein content varies from 5.5 to 9.5% which represents 31-35% of total essential amino acids (Table 9). Other acids are found: palmitic, stearic, linoleic, linolenic, arachidic, lignoceric, and behenic. The oil obtained from the seed is used for confectionery, chocolate elaboration, cosmetics, and soap production. It is principally used as a substitute for cocoa butter.[73]

Table 8
Chemical composition of mango almond[43]

Constituent	Amount %
Moisture	40.50
Protein	1.43
Fatty acids	4.92
Fiber	3.96
Carbohydrates	48.19
Ash	0.83

Table 9
Profile of fatty acids in mango almond[73]

Fatty acid			
Systematic name	Traditional name	Abbreviation	%
Hexadecanoic	Palmitic	16:0	9.3
Octadecanoic	Stearic	18:0	39.1
cis-9-Octadecenoic acid	Oleic	18:1 *cis*-9	40.8
cis-9,12-Octadecadienoic acid	Linoleic	18:2 *cis*-9,12	6.1
cis-9,12,15-Octadecatrienoic acid	Linolenic	18:3 *cis*-9,12,15	0.6
Eicosanoic	Arachidic	20:0	2.5
Docosanoic	Behenic	22:0	0.6
Tetracosanoic	Lignoceric	24:0	0.5
–	Not identified	–	0.5

The kernel obtained after decortication of the mango seed is used in India and Indonesia for the production of flour or as a supplement to wheat flour. It is also used as cattle food and fertilizer. Polysaccharide based biopolymer films have been produced using the starch (carbohydrate) from mango seed waste and pectin from tree tomato.[74]

2.4 Citrus Fruit Waste

Citrus waste provides interesting potential precursors for materials manufacture. The world citrus production is divided into four categories; orange (Citrus sinensis), mandarins/tangarines (Citrus nobilis), grapefruit (Citrus paradise), and lemon (Citrus limon)/lime (Citrus aurantifolia). The total production of citrus in 2009-2010 according to the United States Department of Agriculture (USDA)[51] was 82 Tg where 60.7% of production corresponds to oranges, 25.3% to mandarins, 6.7% to grapefruit, and 7.3% to lemons/limes.

Table 10 gives the world orange production which is mostly attributed to five countries who contribute 71% of all world production, Brazil being the largest producer (33%). For mandarin/tangerine production, 64% is produced by China. Grapefruit and lemon/lime have a lower worldwide production. Even though Brazil only produces orange, the quantity of 16.2 Tg makes it the second biggest producer of citrus (20%). The third producer is the EU-27 which includes almost all European countries (12.8%), followed by Mexico (7.2%) and Turkey (3.9%). These five countries produce 71.4% of the total citrus world production.

The citrus peel represents about 15% of the total fruit weight meaning that the world-wide production of total waste from citrus crops is potentially of the order 12.3 Tg per year. From this quantity 7.4 Tg is attributed to orange production, 3.1 to mandarins, 0.8 to grapefruit, and 0.9 to lemons/limes. According to USDA[51] China produces 3.4 Tg of citrus waste, while Brazil produces 2.4 Tg followed by EU-27 with 1.6 Tg, Mexico with 0.9 Tg, and Turkey with 0.5 Tg.

The approximate composition of different citrus peel is presented in Table 11. All provide essential oils and so have been used since ancient times for perfumes and as aromatic substances. Table 12 presents the main compounds: monoterpenes, aldehydes, alcohols, and esters of the oils.

Table 10
World citrus production in 2009–2010[51]

Orange		Mandarin/tangerines		Grapefruit		Lemon and lime	
Country	Production/Tg	Country	Production/Tg	Country	Production/Tg	Country	Production/Tg
Brazil	16.24	China	13.30	China	2.90	Argentina	1.00
China	6.35	EU-27	3.07	Israel	0.25	EU-27	1.16
Egypt	3.57	Japan	1.10	Mexico	0.41	Mexico	2.04
EU-27	6.20	Korea, South	0.70	South Africa	0.35	Turkey	0.68
Mexico	3.45	Turkey	0.75	United States	1.11	Unites States	0.78
World	49.78	World	20.71	World	5.47	World	5.99

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Table 11
Chemical composition of citrus peel

Constituent (%)	Grapefruit[45]	Lemon[46]	Lime[45]	Orange[47]	Mandarin[47]
Dry matter	91.8	89.4	89.9	—	—
Ash	4.2	5.2	5.1	2.6 ± 0.1	5.1 ± 0.2
Crude protein	4.9	9.3	9.7	9.1 ± 0.4	7.5 ± 0.2
Crude Fiber	11.9	14.9	14.4	—	—
Sugars	—	—	—	9.6 ± 0.2	10.1 ± 0.5
Fatty acids[c]	1.06[a]	1.51 ± 0.11[b]	1.24[a]	4.0 ± 0.2	1.6 ± 0.1
Pectin	—	—	—	23.0 ± 2.1	16.0 ± 1.2
Flavonoid	—	—	—	4.5 ± 0.2	5.1 ± 0.1
Lignin	—	—	—	7.5 ± 0.6	8.6 ± 0.8
Cellulose	—	—	—	37.1 ± 3.1	22.6 ± 2.2
Hemicellulose	—	—	—	11.0 ± 1.1	6.0 ± 0.6
Ether extract	1.1	2.8	2.9	—	—
Nitrogen free extract	69.6	67.8	67.9	—	—

[a]These % compositions were extracted from Hosni et al.[75] [b]This information extracted from Marin and Soler-Rivas.[76] [c]Includes terpenes and volatile species.

Table 12
Percentages of constituent in citrus peel oils[77]

Constituent	Orange	Mandarin	Grapefruit	Lemon	Lime
		% of oil			
Monoterpenes	89–91	98	88	81–85	69
D-limonene	83–90	65–68	88–90	72–80[b]	64
α-Pinene	0.5	0.8	1.6	2	1.2
β-Pinene	1	—	—	7.13	1.2
Myrcene	2	2	1.9	2	—
Υ-Terpinene	0.1	—	0.5	10	22
ρ-cymene	—	2.8	0.4	—	1.9
Aldehydes	1.8	—	1.2–1.8	—	—
Heptanal	3[a]	—	4[a]	1	—
Octanal	39[a]	—	16–35[a]	4[a]	—
Nonanal	5[a]	—	7[a]	6[a]	—
Decanal	42[a]	5	43–54[a]	3[a]	—
Citral	0.05–0.2	—	0.06	1.9–2.6	3.1–5.3
Alcohols	0.9	—	0.3–1.3	—	—
Octanol	2.8	—	—	1	—
Decanol	—	—	—	—	—
Linalool	5.3	2	0–3[b]	—	—
Ester	2.9	—	3–4	—	—

[a]% of total aldehydes, [b]% of total terpene fraction

Different studies show variations in the percentage concentration of oil in the peel as it is influenced by the country of origin, the species, the harvesting season, meteorological, and environmental factors. The results can also be affected by the analytical method used for the extraction[75] but on average, the percentage of oil in the grapefruit, lemon, lime, orange, and mandarin are 1.0, 1.5, 1.2, 4.0, and 1.6%, respectively.

Most citrus peel wastes are used for cattle feed and the rest is disposed, creating a large quantity of natural residue waste.[46] For these reasons in the last few years there have been various initiatives to explore alternative uses. Citrus peels can be used as natural sources of customized functional fibers.[47] Specifically, for orange peel there are initiatives to use them as fermentation substrates for fungal multienzyme production[78] and as a source of Xanthophyll pigment for the improvement of egg yolk color.[79] Researchers from Spain have been working on the generation of bioethanol from pretreated mandarin peel wastes, with steam explosion, due to the high content of carbohydrates.[80] They are also employed as a renewable source for pectin production which is used in the food and pharmacological industry.[81] The conversion of limonene to polymer precursors is disucssed in section 3.1.6.

2.5 Grape Waste

The total world production of grapes (*Vitis vinifera*) is around 15 Tg per year and the main producers are listed in Table 13. According to the Organisation Internationale de la Vigne et du Vin (OIV) (2007),[82] 65% is used for wine and juice (9.8 Tg), 23% as fresh fruit (3.5 Tg), and 12% as dried fruit (1.8 Tg).

The main wine producers (2010 data)[83] are France, Italy, and Spain, sometimes known as the "Big Three" of wine. Approximately 30 kg of waste is produced in the production of 100 L of wine and each litre of wine needs on average 1.3 kg of grapes so that 23% of the grapes used become available waste.[84] The quantity of grapes used in wine production varies with the year and the vineyard. Regarding the production of champagne, according to INAO's (Institut National des Appellations d'Origine) regulations, the obligatory proportion has to be 160 kg/100 L and 150 kg/100 L for sparkling wines. From the available information, during 2009, 2.6 Tg of wine residue, also known as marc or pomace, was produced for which a range of uses have been proposed.[85]

Grape solid wastes comprise mainly skins, pulp, pip, seeds, stems, yeast, and juice that are left after each part of the wine process. A standard process for white wine is presented in Fig. 3 showing the different types of residues produced in each stage of the process. The first grape pressing yields marketable wine and avoids over-pressing of the raw material. Winemakers send the alcohol produced from the remaining pomace to other industries,

Table 13
Main grape producers (2009-2010)[82]

Country	Production/Tg
Brazil	1.30
Chile	1.03
China	5.62
EU-27	2.00
Turkey	2.00
World	15.08
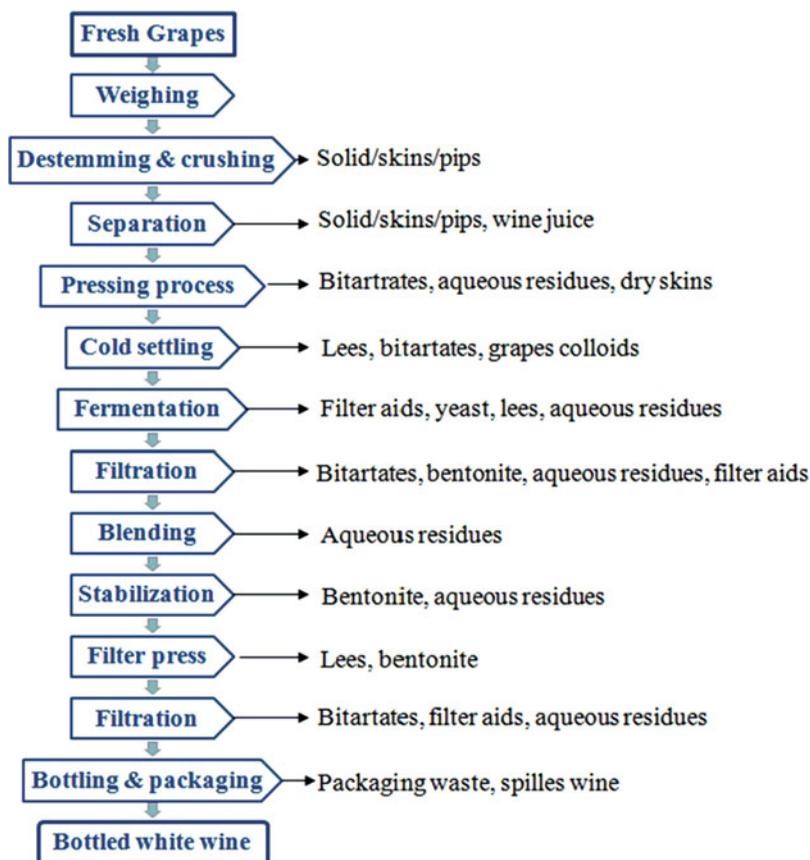
Figure 3. Scheme for conventional white wine production. Modified from Musee et al.[86] with permission from Elsevier (Color figure available online).

a part of the process known as "prestation d'alcool vinique." The last pressings can be discarded or used for vinegar or brandy. In brandy production, the grape marc must be fermented separately from the juice.

Over-pressing of the grapes gives an astringent liquid and an acid juice which are undrinkable making them undesirable products. For this reason continuous pressing is proscribed. The maximum limit to which the pomace is pressed is until oil is obtained.

Grape seed oil contains about 10–20% of oil which is rich in unsaturated fatty acids such as linoleic acid (69–78%, w/w) which contributes to the production of biodiesel (Table 14). The biodiesel quality depends on the fatty acid composition of the oil: unsaturated fatty acids help improve its low-temperature properties.[87]

Grape seeds also contain substances with antioxidant properties such as tocopherols in a range from 240–410 ppm, polyphenols, and oligomeric proanthocyanidins (OPC) which have medical and cosmetic applications. Polyphenolic compounds with antioxidant properties are present in the skin of red grapes but the quantity varies according to the grapevine, cultivar, season, and environmental factors (Table 15). The most abundant compounds are: 3-acetylglycosides, 3-glycosides, 3-p-coumaroylglycosides of malvidin (Mv), peonidin (Pn), delphinidin (Dp), petunidin (Pt), cyaniding (Cy), and tartaric esters of

Table 14
Fatty acids founded in grape seed oil[85]

Fatty acid			
Systematic name	Traditional name	Abbreviation	%
Hexadecanoic acid	Palmitic	16:0	5–11
cis-9-Hexadecenoic acid	Palmitoleic	16:1 *cis*-9	0.5–0.7
Octadecanoic acid	Stearic	18:0	3–6
cis-9-Octadecenoic acid	Oleic	18:1*cis*-9	15–20
cis-9,12-Octadecadienoic acid	Linoleic	18:2 *cis*-9,12	69–78
cis-9,12,15-Octadecatrienoic acid	Linolenic	18:3 *cis*-9,12,15	0.3–1

hydroxycinnamic acids, monomeric and dimeric flavanols, flavonols, and stilbenes. The other principal use of red wine waste is the solid-liquid extraction of anthocyanin pigments which are used in the cosmetics, food, and the pharmaceutical industry.[88]

In contrast to many food wastes, a wide range of industries already benefit from grape waste including composting, dietary supplements, gas production for heating purposes, pharmaceutical additives, and animal feedstuffs. It can therefore be argued that with this extensive waste utilization program already underway, grape waste does not provide a strong and unique opportunity for obtaining chemical precursors for other uses.

2.6 Pumpkin Seed

Also known as pepitas in many countries, pumpkin seeds are cooked and eaten. The seed represents approximately 20% of the total weight of the pumpkin, and according to Table 16, which lists the main suppliers the annual production of seeds is 4.2 Tg. The main consumers of pumpkin seeds are countries from Latin America, notably Mexico and Central America and Asian countries due to their type of cuisine, traditions, and diet.

Pumpkin seeds are also a source for natural oils which are very rich in unsaturated fatty acids (up to 78%) (Table 17). Expected therefore to be vulnerable to oxidative degradation, it is found experimentally to be a vegetable oil with high oxidative stability partly because of the low 18:3 and high 18:1 contents, partly the high δ-tocopherol content which absorbs free radicals and partly the low fraction of sterols in the oil. Sterols are fatty acid esters that can be hydrolyzed producing free fatty acids promoting the autoxidation sequence.

Table 15
Phenolic substances in grape seeds[85]

Antioxidants	g L^{-1}	g per 100 g dry matter
Total phenols (GAE)	2.86 ± 0.01	8.58 ± 0.03
Total flavanoids (CE)	2.79 ± 0.01	8.36 ± 0.04
Proanthocyanidins (CyE)	1.38 ± 0.06	5.95 ± 0.17

(GAE: gallic acid equivalent; CE: catechin equivalent; CyE: cyanidin equivalent)

Table 16
Word production of pumpkins in 2009[51]

Country	Production/Tg
China	6.5
Russian Federation	1.23
United States of America	0.75
Egypt	0.7
Ukraine	0.56
World	21.2

2.7 Sugar Bagasse

Sugar cane (*Saccharum L.*) is mainly cultivated for sugar and ethanol production and world production in 2010–2011, was 130 Tg, with Brazil and India being the main producers with 50% of total production (Table 18).

The processing of sugar cane is divided into two stages—milling and refinery. Milling involves extraction of the raw sugar by crushing the canes between rollers to obtain a white juice with 15% sugar. Through different methods, mainly evaporation and centrifugation, the juice is purified into a raw sugar containing 60% sucrose after which the refining process purifies and concentrates the sugar to 99% sucrose by boiling in a vacuum pan.[90] The industrial waste from milling is the sugar cane remaining, known as sugar bagasse, and represents 28% of the dry weight of the original. The main constituents of the sugar bagasse are glucan (39%), lignin (25%), and xylan (22%) (Table 19). Annual production of bagasse is thus approximately 36.5 Tg and much is currently used in distillery plants as a source of energy, for pulp and the paper industry, for the production of particle board, fiber board, cardboard, furfural, microcrystalline cellulose, hydrolysed bagasse, pre-digested pith, molasses-urea-pith, furfural cement, and compost.[91]

Sugar cane is a lignocellulosic material and hence an attractive feedstock for ethanol fuel production. It is mainly composed of lignin (20–30%), cellulose (40–45%), and hemi-celluloses (30–35%).[92] The limiting step is the degradation of cellulose and hemicelluloses

Table 17
Fatty acids in pumpkin seed oil[89]

Fatty acid			
Systematic name	Traditional name	Abbreviation	%
Hexadecanoic acid	Palmitic	16:0	6.2
Octadecanoic acid	Stearic	18:0	1.9
cis-9-Octadecenoic acid	Oleic	18:1 *cis*-9	32.6
cis-11-Octadecenoic acid	cis-Vaccenic	18:1 *cis*-11	0.6
cis-9,12-Octadecadienoic acid	Linoleic	18:2 *cis*-9,12	58.2
cis-9,12,15-Octadecatrienoic acid	Linolenic	18:3 *cis*-9,12,15	0.2
Eicosanoic acid	Arachidic	20:0	0.1
cis-11-Eicosenoic acid	Gondoic	22:1 *cis*-11	0.1

Table 18
World production of sugar cane during 2010/2011[51]

Country	Production/Tg
Brazil	39.40
China	11.72
India	25.70
Mexico	5.45
Thailand	6.87
World	130.43

into sugars for ethanol production which is complex, energy-consuming, and has a high cost. Clearly, the main source for bioethanol is the primary sugars but this prompts competition over land use between food and the biofuel production.[91] The production of ethanol from sugar cane bagasse is more complex involving five processes—biomass pre-treatment, cellulose hydrolysis, fermentation of hexoses and pentoses, separation and effluent treatment (Fig. 4).[92] The biomass pretreatment is based on the solubilization and separation of the components needed (polysaccharides and carbohydrates) for their further treatment. Subsequent hydrolysis breaks the hydrogen bonds of the major molecules into their sugar components, which are then fermented into ethanol.[93]

The importance of the ethanol route is that ethanol can undergo an acid catalyzed dehydration to ethene, which can enter directly into a conventional chemical process plant. It can be converted into polyethylene and used in the synthesis of vinyl chloride and for the production of styrene and hence to their polymers.

2.8 Coffee Waste

World coffee (*Coffea sp.*) production exceeds 8.4 Tg and there are two main varieties, *Coffea arabica* and *Coffea robusta.* Brazil and Vietnam are the main producers controlling 53% of world total production (Table 20).[51]

Table 19
Chemical composition of sugar cane bagasse[44]

Constituent	%
Glucan	39
Xylan	21.8
Galactan	0.8
Arabinan	1.8
Acetyl	3.3
Lignin	24.8
Ash	3.9
Protein	0.5
Sucrose	0.7
Water extractives	2.7
Ethanol extractives	1.9
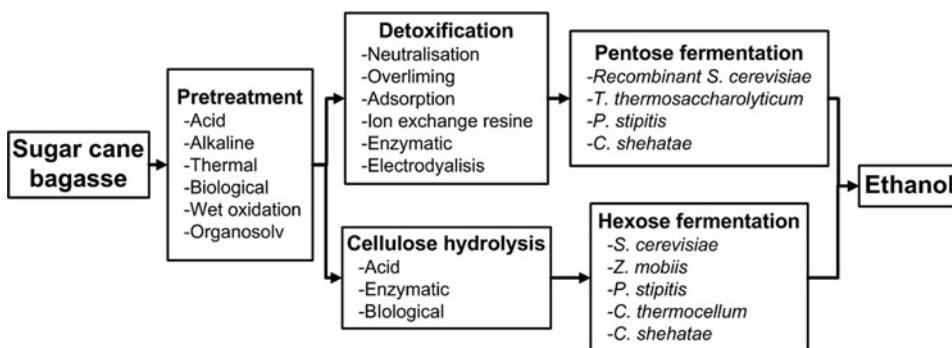
Figure 4. Industrial process for fuel ethanol production from sugarcane bagasse. Reproduced from Cardona et al.[92] with permission from Elsevier.

The industrial process to obtain isolate coffee powder consists of removing the shell and mucilaginous part of the cherries[94] by either a wet or dry process, each producing wastes with different compositions. Endocarp, mesocarp, and exocarp from the dried fruit represent 60% of total weight, that is, 5 Tg of coffee waste are produced each year where 55% comes from Latin America where there are as yet no industrial uses for it.

Coffee husk and pulp chemical compositions are shown in Table 21 although clearly, these vary with plant, cultivation conditions, and crop. The residues still have a significant percentage of caffeine which restricts their subsequent use while tannins inhibit its use as cattle feed because of counter-nutritional effects. Solution treatments and ensilage diminish the amount of anti-nutritional substances like polyphenols, tannins, and caffeine.[95]

Through biotechnology processes, coffee wastes are used to produce enzymes such as pectinase, tannase and caffeinase, flavor, and aroma compounds used in the food industry. It is also used in the cultivation of mushrooms, for biogas production by anaerobic digestion and for composting.[50] Applications involving a bioconversion process generally need detoxification of tannins and caffeine in the coffee residues as a prerequisite. The latest applications include the use as fibers for the production of particle board[96] and as a source for the synthesis of SiO_2 nanoparticles.[97]

Table 20
Coffee world production, 2010/2011[51]

Country	Production/Tg
Guatemala	0.24
Mexico	0.28
Brazil	3.32
Colombia	0.54
Peru	0.24
India	0.28
Indonesia	0.58
Vietnam	1.12
Ethiopia	0.25
Uganda	0.19
World	8.38

Table 21
Chemical composition of coffee waste[50]

Constituents	[a]Coffee pulp wt.% DM		Coffee husk wt.% DM
Carbohydrates	50	44	57.8
Proteins	10	12	9.2
Fibers	18	21	—
Fat	2.5	—	2
Caffeine	1.3	1.3	1.3
Tannins	1.8-8.6	—	4.5
Polyphenols	—	1	—
Pectins	—	—	12.4

[a]Information from multiple sources.

2.9 Banana Waste

Banana (*Musa sapientum*) is one of the most well-known and popular tropical fruit in the world and it is available throughout the year. The peel represents 40% of the banana fruit[98] generating annually around 22 Tg of peels much of which is domestic waste. The four main producers are India, Brazil, Ecuador, and China (Table 22) who generate 27 Tg of bananas per year, being practically 50% of the worldwide output and thus produce 10.9 Tg of potential banana wastes.

The chemical composition of the peel varies with the stage of maturation. Increasing soluble sugar, protein, and lipid content and decreasing hemicellulose and starch take place over time. The degradation of starch and hemicelluloses by enzymes explains the late stage increase of sugar.[99] The general chemical composition of banana peel is shown in Table 23. The high content of protein (7.9%) and carbohydrates (59.5%), make it suitable for fungus cultivation and the high fraction of fatty acids (11.6%) indicates it can be used as an alternative source of energy and potentially for biopolymers. The ash has high levels of phosphorus, potassium, sodium, and magnesium and low levels of calcium and iron.

Banana peel is a source of pectins and dietary fiber.[100] It can be used for mycological research as a medium and as a substrate for microfungal biomass production.[53] From the biomethanation of banana peel, it is also possible to obtain methane[101] by fermentation using flocculating yeast to provide continuous ethanol production,[102] and it is used for the

Table 22
World production of bananas in 2000[98]

Country	Production/Tg
India	11
Brazil	6.3
Ecuador	5
China	4.8
Philippines	3.6
Indonesia	3.2
World	55.2

Table 23

Constitution of banana peel (a) and mineral content of banana peel (b)[53]

(a)

Constituent	Dry Matter %
Dry matter	14.1
Crude protein	7.9
Crude fat	11.6
Crude fiber	7.7
Total ash	13.4
Carbohydrate	59.5
Moisture	78.4

(b)

Constituent	*mg*/100 *g*
Ca	7
Na	34
P	40
K	44
Fe	0.9
Mg	26
S	12
Ascorbic	18

treatment of wastewater plants as an adsorbent for impurities like heavy metals.[103] It is also used as cattle feed, as fertilizer due to the high content of ash, and for the extraction of banana oil, pentyl ethanoate (amyl acetate).

2.10 Avocado Seed

Avocado (*Persea Americana*) is the fruit of a native Mexican tree and it is mainly cultivated in tropical climates. According to FAO[51] the world production is around 3.9 Tg per year where 76% of the total production is controlled by 10 countries (Table 24). As it originated in Mexico, this country is the biggest producer with 32% of world output.

The avocado fruit comprises a dark green peel, green oily pulp, and a large seed which represents 10-22% of the total weight depending on the species,[104] meaning that it contributes potentially 0.85 Tg of waste. The seed is mainly composed of moisture and carbohydrates, while the remaining 10% is lipids, proteins, ashes, and fiber (Table 25).

The fatty acid composition of the avocado seed is shown in Table 26. It contains 27 fatty acids where 17 are saturated (32% of total fatty acids), 7 are monounsaturated (21%), and 3 are polyunsaturated fatty acids (47%).

Research on avocado seed extract has focused mainly on medical and cosmetic applications. These include studies on the antimicrobial potential,[106] skin and hair aerosol uses,[107] for hepatic collagen solubility,[108] skin collagen-metabolism,[109] and effects on liver disease.[110] Clearly wider applications for fatty acids from avocado seed extract may exist including their deployment in polymerization (See Section 3.1.6).

Table 24
World production of avocado 2009[51]

Country	Production/ Tg
Mexico	1.23
Chile	0.33
USA	0.27
Indonesia	0.26
Dominican Republic	0.18
Colombia	0.17
Peru	0.16
Brazil	0.14
China	0.10
Guatemala	0.09
World	3.85

2.11 Carrot Waste

The carrot (*Daucus carota*) is globally the second most popular vegetable after the potato. World production is 33.6 Tg,[51] China being the main producer at 36% (Table 27).

Carrot food waste is made up of peel, the pomace left after juice production, and leaves from harvesting. Approximately 40–30% of carrot pulp is produced after the extraction of juice, leaving a high potential total world production of by-product. The leaf has the major quantity of crude protein and carbohydrates, while the pomace contains more than 60% of fiber. Lipids and ash are present in similar amounts in each of the carrot by-products (Table 28) The by-products are being studied as raw materials for the production of antioxidants. The carotenoids concentrations of α-carotene, β –carotene and lutein and in the carrots pomace are 51, 6, and 36 ppm, respectively.[111]

As with all the other food wastes, carrot leaf is mainly used to complement cattle food. Pomace and peel are used as alternative RACOD (Rapidly Acidifying Chemical Oxygen Demand) source[112] of organic-acids from microbal-production,[113] as a source of soluble-fiber hydrolyzate from enzymatic production[114] and for the removal of chromium from acqueous solutions.[115] The carbohydrate can be used for the production of PLA.[116]

Table 25
Approximate composition of the avocado seed[105]

Constituents	%
Moisture	56.0 ± 2.6
Lipids	1.9 ± 0.3
Protein	2.0 ± 0.2
Ash	1.9 ± 0.2
Fiber	5.1 ± 1.1
Carbohydrates	33.2 ± 2.7

Table 26
Fatty acids found in the avocado seed[105]

Fatty Acid			% of the total fatty acid
Systematic name	Trivial name	Abbreviation	
Saturated fatty acids			32.50
Hexanoic acid	Caproic	6:0	0.80 ± 0.05
Heptanoic acid	Enanthic	7:0	0.29 ± 0.10
Octanoic acid	Caprylic	8:0	0.28 ± 0.05
Nonanoic acid	Pelargonic	9:0	0.22 ± 0.01
Decanoic acid	Capric	10:0	Traces (<0.06%)
Undecanoic acid	Undecylic	11:0	Traces (<0.06%)
Dodecanoic acid	Lauric	12:0	0.28 ± 0.05
Tridecanoic acid	Tridecylic	13:0	0.17 ± 0.01
Tetradecanoic acid	Myristic	14:0	0.54 ± 0.05
Pentadecanoic acid	Pentadecylic	15:0	2.33 ± 0.11
Hexadecanoic acid	Palmitic	16:0	20.85 ± 0.84
Heptadecanoic acid	Margaric	17:0	1.73 ± 0.02
Octadecanoic acid	Stearic	18:0	1.19 ± 0.01
Nonadecanoic acid	Nonadecylic	19:0	0.61 ± 0.34
Eicosanoic acid	Arachidic	20:0	0.04 ± 0.02
Docosanoic acid	Behenic	22:0	1.11 ± 0.02
Tetracosanoic acid	Lignoceric	24:0	1.69 ± 0.05
Monounsaturated fatty acids			20.71
cis-9-Tetradecenoic acid	Myristoleic	14:1 *cis*-9	0.25 ± 0.002
cis-10-Pentadecenoic acid		15:1 *cis*-10	0.32 ± 0.16
cis-9-Hexadecenoic acid	Palmitoleic	16:1 *cis*-9	1.79 ± 0.33
cis-10-Heptadecanoic acid		17:1 *cis*-10	0.37 ± 0.08
cis-9-Octadecenoic acid	Oleic	18:1 *cis*-9	17.41 ± 0.06
cis-11-Eicosenoic acid	Gondoic	20:1 *cis*-11	0.45 ± 0.28
cis-13-Docosenoic acid	Erucic	22:1 *cis*-13	0.12 ± 0.04
Polyunsaturated fatty acids			46.73
cis-9,12-Octadecadienoic acid	Linoleic	18:2 *cis*-9,12	38.89 ± 0.59
cis-9,12,15-Octadecatrienoic acid	Linolenic	18:3 *cis*-11	6.58 ± 0.03
cis-11,14,17-Eicosatrienoic acid		20:3 *cis*-11	1.26 ± 0.03

2.12 Peanut Husk

Peanut (*Arachis hypogaea L.)* is widely harvested and used in most cultures. The worldwide production of peanut in 2011, reached 34 Tg.[51] The grain constitutes about 30%, indicating that 10 Tg of total residues are produced in the form of husks. The five main producing countries are China (14.6 Tg) India (6 Tg), USA (1.8 Tg), and Nigeria (1.6 Tg). The literature differs on the chemical composition of peanut husk[40,117–119] but the most complete version is presented in Table 29.

The incineration of peanut husks has given way to various recycling schemes. The high lignin and low nitrogen contents mean that degradation is difficult to achieve which limits

Table 27
World production of carrot 2009[51]

Country	Production/Tg
China	12.09
USA	1.45
Russia	1.35
Poland	0.94
Uzbekistan	0.82
United Kingdom	0.75
Japan	0.67
Turkey	0.64
Ukraine	0.60
Italy	0.57
World	33.58

their use as fertilizers so the main uses are as feed for cattle, pigs, and birds, as a culture medium for fungi, and for protection of plants.

According to the US Department of Agriculture Chemist, National Peanut Research Laboratory[120] one third (33%) is used as cattle feed, another third (33%) as a base for litter and bedding, 30% functions as a chemical absorbent because when combined with

Table 28
Chemical composition and natural antioxidants of carrot by-products

Constituent (%)	Pomace [55]	Peel [56]	Leaf [57]
Moisture	—	—	7.2 ± 0.1
Crude protein	8.4 ± 0.2	9.7 ± 0.3	15.1 ± 0.5
Crude lipid	1.1 ± 0.1	1.5 ± 0.1	–
Fiber	63.5 ± 1.5	45.5 ± 0.4	12.0 ± 0.3
Ash	7.7 ± 0.01	10.3 ± 0.3	10.5 ± 0.3
Carbohydrate	19.3	33.0 ± 0.8	52.7 ± 0.7
Others	—	—	2.5 ± 0.1
Antioxidants			
β-carotene (mg/100g dry weight)	—	20.5 ± 0.5	8.7 ± 0.3
Total phenolic (mg GAE/100g dry weight)	—	1371 ± 14	—
Total antioxidant activity (% of high dietary fiber powder)	—	96.7 ± 1.2	—
Vitamin C (mg/100g dry weight)	—	—	203.0 ± 3.8

Table 29
Peanut husk composition[119]

Constituent	Weight%
Lignin	34.8
Glucan	21.1
Extractives	14.2
Protein	11.1
Xylan	7.9
Ash	3.4
Arabinan	0.7
Galactan	0.2
Mannan	0.1
Others (e.g. free carbohydrates)	6.5

activated carbon it helps remove offensive tastes, odors, colors, chlorine, and organics substances and the remaining 3% is mainly a source of hydrogen for fuel cells. In some countries, notably China, the shells are used as a biomass fuel in stoves and boilers as a replacement for coal. It is claimed that peanut shell provides higher energy efficiency than traditional coal boilers as well as being cheaper to operate.[121] A catalytic pyrolysis process for the production of renewable hydrogen from peanut shells is available.[122] In another application, the fibrous skeleton that supports the cellulosic layer of the peanut husk can be used in the form of nonwoven biodegradable fabrics to control soil erosion until vegetation is matured.[123] Peanut shells are also employed for the absorption of toxic metal ions including cadmium copper, nickel, lead, and zinc from solution[124] and in the treatment of industrial wastewaters.[125] In comparison with pine sawdust, a common copper remover in industry, peanut husk removes 98% of copper ions from wastewaters while pine sawdust removes only 44%.[126] Peanut shell waste is mainly composed of fiber and is used as such in the form of reinforcement in polymer composites while the oil obtained from the seed can be polymerized.

2.13 Cereals Straw

According to FAO in 2011, the worldwide production of cereals was of 2.6 Pg. This category includes the production of wheat, rice paddy, barley, maize, popcorn, rye, oats, millets, sorghum, buckwheat, quinoa, fonio, triticale, canary seed, mixed grains (mixture of cereal species that are sown and harvested together), and minority cereals (cereal crops that are not identified separately because of their minor relevance at the international level).[51] The top producer countries are shown in Table 30. China is the main producer with 20% of the world production, followed by USA and India with 15% and 11%, respectively. These three countries produce 42% of worldwide production.

The cereal crop residues after harvesting compromise 50-75% of the total production.[127] This indicates that at least 2.6 Pg of residues are produced after harvesting the crops. In Table 31 is presented the composition of wheat straw as an example of the straws obtained from cereals. It can be seen that these residues mainly contain fiber, cellulose, and hemicelluloses.

Table 30
Cereals production in 2011[51]

| Country	Production/Tg
China	520.9
USA	386.8
India	285.5
Russia	91.8
Indonesia	83.4
Brazil	77.6
France	65.7
Ukraine	56.3
Bangladesh	52.6
Argentina	50.9
World	2587

Some of this residue is left on the soil in order to reduce its erosion and as fertilizer as it reincorporates organic matter in the soil.[127] It is also used for the production of waxes by CO_2 extraction[128] for their use in cosmetics, polishes, or the coating industry, and as a biofuel in energy plants where it is burned in order to produce high pressure steam which is used to drive a turbine to generate electricity,[129] the use of the lingo-cellulosic material to produce strawboards,[130] as fire-retardant of wood,[131] and their use in the construction industry.[132] They are also used as reinforcements for different materials, especially for polymers; this is further explained in section 4.

2.14 Animal Waste

Article 3 of Regulation (EC) 1069/2009 of the European Parliament and the Council of the European Union restricts the use and controls the disposal of animal by-products. Such wastes include catering waste, used cooking oil, former foodstuffs, butcher and slaughterhouse waste, blood, feathers, wool, hides, shells and skins, fallen stock among others. These wastes are given three categories for disposal of which Category 3, low risk materials, includes the remains of animals, which are approved for human consumption, after passing through slaughterhouses. These parts are not eaten (bones, feathers, blood,

Table 31
Chemical composition of wheat straw[52,127]

Constituent	% weight Dry matter
Protein	7.8 ± 2.2
Fiber	54.6 ± 0.61
Lignin	4.2 ± 1.3
Cellulose	28.0 ± 0.59
Hemicellulose	22.3 ± 0.76
Straw: grain ratio	1.7:1
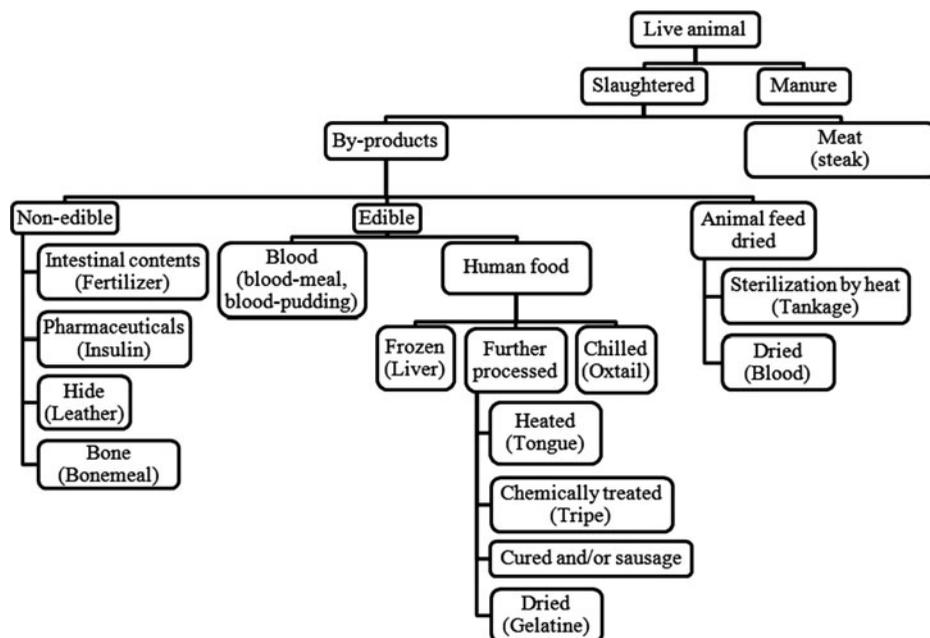
Figure 5. Schematic pathways for industrial meat and by-products. Modified from the Department for Environment Food and Rural Affairs.[133]

skin, hair, shells) or are discarded for commercial reasons and include the waste from food factories and retail premises.[133] Figure 5 shows the by-products from the meat industry.

Some inedible by-products are treated for animal feed, fertilizer or protein based adhesives. Some tissues are used to produce composite bone-cum-protein meals or individual products like bone-meal, meat-meal, and blood-meal. The total amount of waste is 10–15% of the live weight killed (LWK) animal.[134] In 2011, the worldwide meat production, according to USDA, reached 244 Tg where 42% corresponds to pork, 35% to poultry, and 23% to beef.[135] Approximately 25 Tg of category 3 meat waste is produced annually in the world.

One application is the use of fat and oils for the production of biofuels. Triacylglycerols comprised of three long-chain fatty acids can be hydrolyzed or transesterified to acids or esters and glycerol. The esters can be used as biodiesel once the glycerol is removed.[136] Other waste which is studied for its exploitation is the feathers which can be used for the production of biodegradable thermoplastic films though graft polymerization with methyl acrylate.[137]

In the case of seafood, the shellfish catch consists approximately of 30% crustaceans and 70% molluscs. Crustacean processing waste compromises 40% exoskeletons (shell) while the mollusc processing waste consists of 65% shells.[138] In 2010, 20.8 Tg of mollusc and 11.8 Tg of crustaceans where caught, producing 18.2 Tg of shell waste.[51] This waste contains approximately 10% of chitin on dry weight.[139]

3. Strategies for Production of Biopolymers from Food Waste

The second part of this review explores how this huge resource might be exploited by making use of some of its constituents for the production of polymers with an emphasis on hydrophobic polymers, routes to hydrophilic polymers having been well explored and reviewed in previous work in this journal.[19,24] Figure 6 shows the main pathways (direct
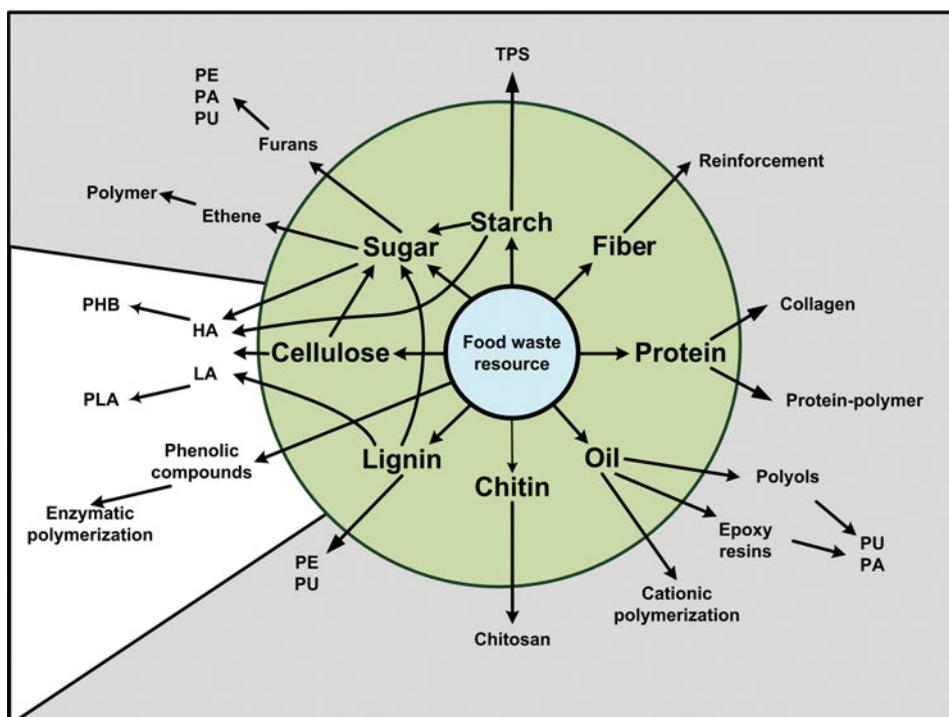
Figure 6. A schematic chart of the categories of biomass-sourced polymers showing the direct and indirect paths to hydrophobicity. Sugar has to be first converted into ethanol in order to obtain the ethene monomer. PE = polyester, PU = polyurethane, PA = polyamide, TPS = thermoplastic starch, HA = hydroxyalkanoates, LA = lactic acid, PHB = polyhydroxyalkanoate, PLA = poly lactic acid (Color figure available online).

and indirect) from the food waste resource, in some cases passing through hydrophilic polymer precursors, to the monomer which can be converted to hydrophobic polymers. The main goal is to reach, at the end of the process, a polymer which can act as a competitive replacement for the mineral oil-derived equivalent.

There are three basic strategies for the production of polymers which are designed to finish their useful life in composting, incineration, or biodegradation.[140] The lifecycles for such materials are illustrated in Fig. 7. The traditional strategy is the direct use of biomass (wood, straw, cork) or biomass components (fibers, natural rubber, starch, cellulose, sugar, oils) in a finished product via physical changes such as mixing or chemical changes such as crosslinking. Much current interest is focused on a higher level of human intervention in the conversion of biomass resources by isolating monomers or oligomers to generate new compounds by industrial biotechnology involving chemical methods or fermentation (white biotechnology). Looking to the future, the strategy that seems likely to become more important especially to achieve enhanced yields, is the development of transgenic plants for production of biopolymers or polymer building blocks.

3.1 Biomass-Sourced Polymers

The first three classes of raw material are starches, celluloses, and chitin which fall under the general heading of polysaccharides, carbohydrates formed by the condensation of monosaccharide residues through hemi-acetal or hemi-ketal linkages. They can also be
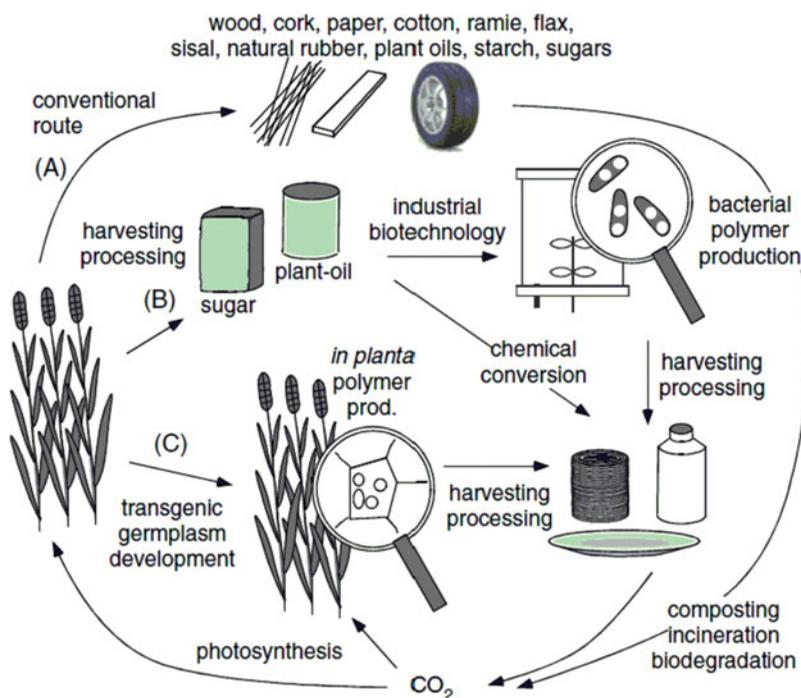
Figure 7. A pictorial representation production cycles for biodegradable polymers from reference. Reproduced from Beilen and Poirier[140] with permission from Wiley (Color figure available online).

found as short oligosaccharide sequences or polymeric repeat units linked to other biopolymers. They are biopolymers which are extracted directly as raw materials from plants and animals. Organisms use polysaccharides for energy storage and structural components.[141] The major representative macromolecules on this sector are cellulose fiber, chitin film and starch granules, and together they make-up around 22 to 37% of food waste resources as shown in Tables 1 and 2.

Although they are known as the unmodified polymers, they generally need to have a bulk or surface chemical modification, mainly on the hydroxyl groups of their backbone structure for their use as biopolymers. The bulk modification relates to the formation of derivatives, of which chitosan is an example, while surface modification involves compatibility and minimization of hydrophilicity of natural fibers through covalent bonds between the surface and the matrix of the fibers.

The modification of natural polysaccharides has mainly focused on reducing hydrophilicity (hydrophobization) by lowering the surface energy or by creating an adequate surface morphology to obtain a water contact angle higher than $90°$.[142,143]

3.1.1 Starch. Starch is produced from agricultural plants, mainly from potatoes, rice, maize, and wheat in the form of hydrophilic crystallites with dimensions ranging from 1 to 100 μm. It appears as a food waste, however, mainly in potato and to a lesser extent mango seed. It is a hydrocolloid biopolymer comprised of two types of α-glucan: amylose (poly-α-1,4-D-glucopyranoside) a linear polymer and amylopectine (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside) as shown in Fig. 8.[144,145] Depending on the botanical source, the percentage of each polymer varies, as well as the morphology, molecular structure, and
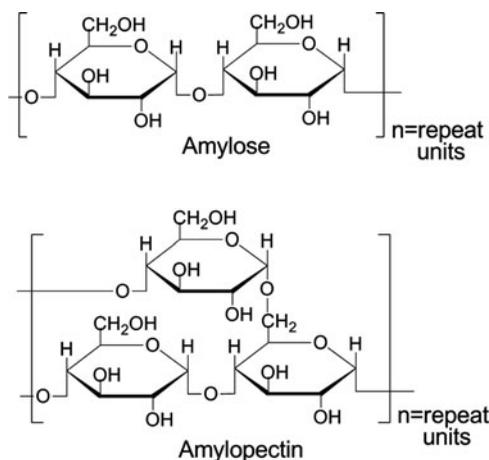
Figure 8. Structure of starch.

composition, affecting the properties of the extracted starch. The most well-known source of starch is the potato which according to Table 1 contains around 67 wt.% starch.

Starch rich in amylose is preferred in different processes because its linearity guarantees better flow properties and an increase in elongation and strength.[146,147] Starch stability is broken when: (i) it is heated at 150°C where the glucoside links start to break, (ii) at 250°C due to the collapse of structure, and (iii) at low temperatures when the retrogradation of starch takes place (amylase and amylopectin reorganize themselves causing gelatization of starch).[148]

Starch can be used in its natural form, mixed or as a filler for, *inter alia*, the formulation of tablets and capsules, for medical prosthesis, or to enhance paper performance. For use in its natural form it should be modified to overcome the poor thermal, shear, and acid stability as well as high rates and extents of retrogradation. It has two available functional groups for modification; the nucleophilic hydroxyl groups and ether bonds. Starch can be chemically modified; for example, partial acid hydrolysis on the amorphous regions of the starch granules generate starch nanocrystals,[149] or physically modified by hydrothermal treatment, where the starch structure and properties are changed without destroying its granular structure.[150] In the case of starch-filled polymer systems, starch should also be modified to develop compatibility between the starch and the synthetic polymers.[151]

To be used as a thermoplastic matrix, the granular structure of starch has to be destroyed through chemical methods, heat treatments, water absorption, or thermomechanical treatment, such as extrusion, to form a homogeneous amorphous phase. Thermoplastic starch (TPS) can also be prepared in the presence of plasticizers like polyols, glycerol, fructose, xylitol, sorbitol, maltitol, ethanolamine, formamide, and urea which promote starch granule destruction by breaking the hydrogen bonds in the crystallites.[24] TPS has enormous advantages as it is cheap, abundant, and biodegradable but it has two major disadvantages, the poor mechanical strength properties and high moisture sensitivity.[152] There are some solutions for this;[143] TPS can be mixed with appropriate fillers like nanoparticles, the surface can be chemically modified, or it can be blended with a hydrophobic polymer;[148] such as polyvinyl alcohol,[153] poly(ethylene-co-vinyl alcohol), PLA, polycaprolactone (PCL), poly (butylenes succinate) (PBS), polyhydroxybutyrate (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).
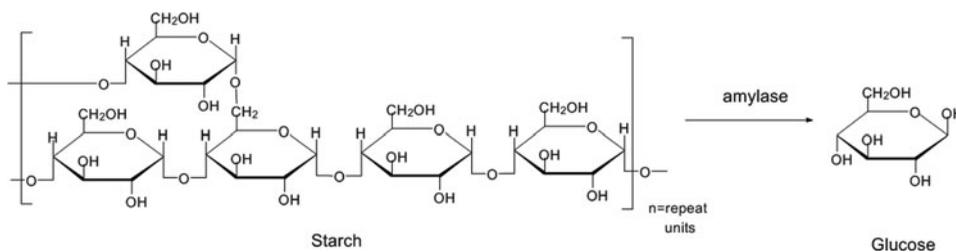
Figure 9. Hydrolysis of starch into sugars.

Starch biodegradation is accomplished by enzymatic hydrolysis of the acetal linkage. The α-1,4 link is attacked by amylases while the α-1,6 is cleaved by amylo-glucosidases, breaking down the starch structure into sugars (Fig. 9). When α-amylose is used, a combination of maltotriose, maltose, and dextrins are obtained as it attacks the starch structure randomly, while β-amylase works at the end of the polymer hydrolyzing the second α-1,4 glycosidic bond producing two-glucose sugar maltose and γ-amylase attacks the α-1,4 glycosidic bond at the end of the amylase producing glucose.[154] The sugars obtained can be subsequently dehydrated to furfural derivatives for the production of furans, which is explained below in section 3.1.7.

The release of hydrolysis products varies according to the botanical origin, chemical or physical previous modification, granule integrity, crystallinity, porosity, amylase and amylopectin rate, structural inhomogeneities, phosphates, protein, and lipids content.[155]

3.1.2 Cellulose. Cellulose is a linear polymer with repeating units of anhydro-D-glucopyranose (cellobiose) where each monomer contains three hydroxyl groups (Fig. 10). It is a highly crystalline and high molecular weight biopolymer. Cellulose is characterized by its poor solubility due to the strong intra- and inter-molecular hydrogen bonds within and among the individual chains. The reactivity of cellulose is affected by the morphology and degree of crystallinity, which vary according to the origin and pretreatment of the material.[156] As summarized in Tables 1 and 2, food wastes which contain cellulose in high concentrations are peanut husks, citrus peels, straw, and corn stover.

The macroscopic morphology of cellulose is always in the shape of fibers. Cellulose fibers are used as reinforcements, replacing glass fiber in composite materials with thermoplastics or thermosetting polymer matrices. They offer the advantages of reduction in density and cost, lower fiber abrasion on processing machinery, the ubiquitous availability of lignocellulosic fibers, recycling opportunities, or combustion for energy recovery; procedures which cannot be applied to glass fiber.[143]
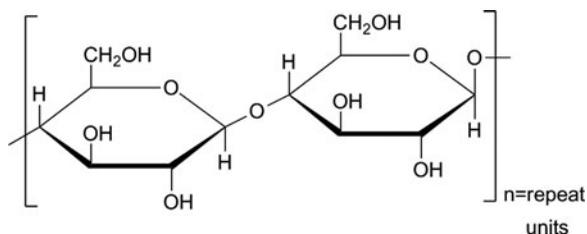
Figure 10. Structure of cellulose.
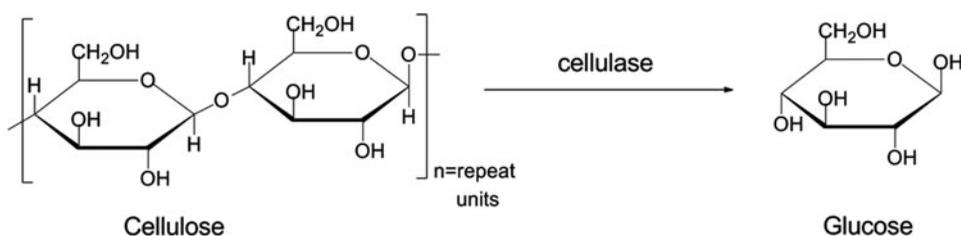
Figure 11. Hydrolysis of cellulose into glucose.

Surface chemical modification is used to improve adhesion between the polar OH groups of the cellulose fiber and non-polar polymer matrices; the ideal solution is to create covalent bonds between the fiber surface and the matrix. Chemical modification reduces hydrophilicity and hence moisture absorption of cellulose fiber.[143] The most common derivatives from the modification of one or more hydroxyl groups in the cellulose structure are ethers, esters, and acetals; such modified materials being already commercially available.[148]

There is extensive research on both chemical and physical modification. Examples of chemical modification for the papermaking industry are cellulose ester elaboration, trans-esterification reactions, esterification of cellulose nanofibers, and cellulose silylation. Physical modifications include surface treatment with cold-plasma, grafting of reactive natural products, coating cellulose with different polymers without covalent attachments or with titanium dioxide followed by an alkyl-chain silica layer produced by sol-gel chemistry.[142]

Native cellulose does not have thermoplastic properties but through mechanical treatment it is possible to obtain plastic properties in cellulose fibers, useful for the manufacture of films based on cellulose. On the other hand, chemical modification such as esterification of hydroxyl groups with acids on the cellulose structure confers new properties of flow, resistance, and durability comparable to those of a synthetic plastic. Also, more resistant materials with improved durability can be achieved by the chemical grafting of biopolymers. The formation of covalent links between the chains from the hydrophilic functions diminishes the hydration possibilities and flow properties while increasing cohesion.[24] As explained previously in section 2.2, cellulose can be turned into polyols by liquefaction processes for the production of polyurethane[72] foams and polyesters.[71]

Cellulose degradation can be achieved by enzymes secreted from fungi, bacteria, and protozoans which catalyze the oxidation reactions of cellulose, or lower molecular weight oligomers produced from the enzymatic hydrolysis of cellulose.

The hydrolysis by cellulose enzymes decomposes the cellulose structure into glucose (Fig. 11). Some examples of such enzymes are the endo-1,4-β-glucanase which attacks the internal bonds and the exo-1,4-β-glucanase which attacks the end of the cellulose structure and separates the cellobiose into two glucose moieties.[154]

Other examples are the peroxidases which provide hydrogen peroxide for the free radical attack on the C2-C3 positions of cellulose to form aldehydes followed by their hydrolysis to form lower molecular weight fragments. Bacteria produce endo- and exoenzymes which form complexes that degrade cellulose into carbohydrates which are used by microorganisms as nutrients. The final products from aerobic biodegradation are carbon dioxide and water while anaerobic degradation produces carbon dioxide, hydrogen, methane, hydrogen sulphide, and ammonia.[35,157] Methane emissions resulting from this degradation promote climate change particularly in the case of disposal to landfill. When it
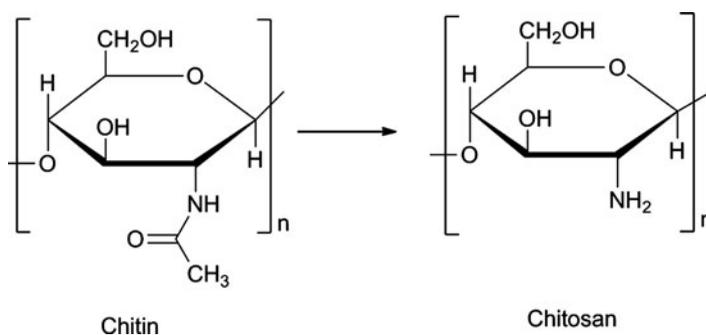
Figure 12. Chitin and chitosan chemical structure.

is composted it decreases the need for peat extraction and restricts such gas emissions. As with many biodegradable polymers, the environmental effect may vary depending on the disposal method applied.[158]

3.1.3 Chitin. Chitin is a polymer found in crustacean and insect exoskeleton, and can also be found in mushrooms and yeasts. As mentioned in section 2.14, the main source is from sea food processing waste which produces around 18 Tg of shell waste.

It is a linear cationic heteropolymer of (1-4)-linked *N*-acetyl-β-D-glucosamine (Fig. 12). Because chitin has an intractable character and very poor solubility, its direct uses as a macromolecular material are limited. However, it can be chemically modified by partial alkaline *N*-deacetylation at high temperatures which generates the corresponding primary amino function. The percentage conversion of acetyl glucosamine to glucosamine is described as the degree of deacetylation. This influences the physical, chemical, and biological properties.[159]

Chitosan, the *N*-deacetylated product of chitin, is only accepted when the degree of deacetylation permits its solubility in acidic media. With 40% level of acetylation, the polysaccharide chains become moderately soluble, forming stable aggregates in which the *N*-acetyl groups are unevenly distributed. When it is higher than 60% it becomes insoluble and acquires structural flexibility.[160]

The derivative chitosan is somewhat the opposite of chitin; due to its rigid crystalline structure, strong hydrogen bonding, and free protonable amino groups it is soluble in mildly acidic aqueous solutions and insoluble in water and alkaline media.[161] It can be chemically modified at either or both the amino and hydroxyl functions for further applications while chitin only has two hydroxyl groups to be modified (Fig. 12). The modifications of chitin and chitosan do not change the original physicochemical and biochemical properties.

There are several reviews on the chemical modification of chitin and chitosan.[162–164] Some examples are: modification through graft copolymerization with polymers like polyurethanes, poly(2-alkyl-oxazolines), poly(ethylene-glycol)s, block polyethers, poly (ethylene-imine)s, poly(2-hydroxyalkanoate)s, poly(dimethylsiloxane)s, and dendrimer-like hyperbranched polymers.[162] It can also be chemically phosphorylated,[163] acylated, and alkylated, a Schiffs base formed and then reduced, carboxylated, phthaloylation, silylated, tosylated, and the quaternary salt formated, sulfated, and thiolated.[164]

Chitosan can be molded as fibers,[161] films,[165] or precipitated in different micromorphologies from its acidic aqueous solutions. Both substrates, chitin and chitosan, are also
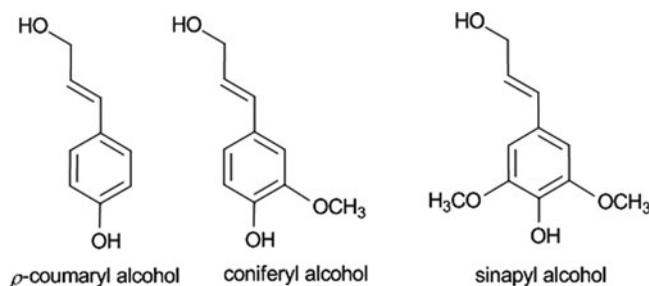
**Figure 13.** Monomers which form lignin complex structure.

being used as antibacterial agents, cell-stimulating materials in animals and plants, hydrogels, blood anti-coagulants, food additives, haemostatic materials, anti-thrombogenic materials, textile material, cosmetic ingredient, for drug delivery, tissue engineering, biocatalyst immobilization, waste water treatment, molecular imprinting, and in metal nanocomposites, etc.[166–171]

The enzyme chitinase is responsible for the degradation of chitin while chitosanase and lysozymes degrade chitosan. They can be depolymerized chemically, enzymatically, or by physical methods. The chemical process is based on an acid hydrolysis with hydrogen chloride or an oxidative reaction with nitrous acid and hydrogen peroxide. In enzymatic processes, chitosan can be depolymerized by enzymes such as chitinase, chitosanase, gluconase, some proteases, lysozyme, cellulase, lipase, amylase, and pectinase. Physical degradation can be achieved by radiation, ultrasound, microwave, and thermal treatments.[169]

The in-vivo biodegradation of chitin and chitosan produces non-toxic oligosaccharides of different lengths which are later incorporated to methabolic pathways to give glycosaminoglycans and glycoproteins or are excreted. The biodegradation rate depends on the degree of acetylation, distribution of acetyl groups, and length of the chain.[168] In the case of medical applications it is important to avoid fast rates of degradation as this can lead to the accumulation of amino sugars which provoke an inflammatory response.[172]

3.1.4 Lignin. Lignin is a three-dimensional network formed by the monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols, Fig. 13.[173] Lignin is a complex highly branched structure and irregular macromolecule in which basic blocks can be defined as "C9" units; however, the structure varies according to the vegetable source. In lignocellulosic materials, lignin is the matrix that surrounds cellulosic fibers.

Lignin is viewed as a waste material, available in large quantities from peanut husks, citrus peels, sugar bagasse, and corn stover (Tables 1 and 2) and is also derived from wood pulp. Commercially, lignins are available as co-products whose main derivatives are lignosulfates and kraft lignins.[174] Their main structure is based on lamellar macromolecular complexes which link through non-covalent interactions.[24] The lignin structure can undergo chemical modification to allow the synthesis of polymers. It can be modified on both the phenolic and aliphatic hydroxyl groups, to prepare polyesters and polyurethanes through liquefaction processes, as previously explained in section 2.2, which used the lignocellulosic material found in the corn stover as feedstock.[71,72] It can also be fragmented into monoaromatic monomers to produce polyether-polyol polymers. Polyols can be obtained through oxypropylation. In general, the polymers obtained from these monomers possess advantageous thermal and mechanical properties due to the present aromatic character, some examples are shown in Fig. 14.[175]
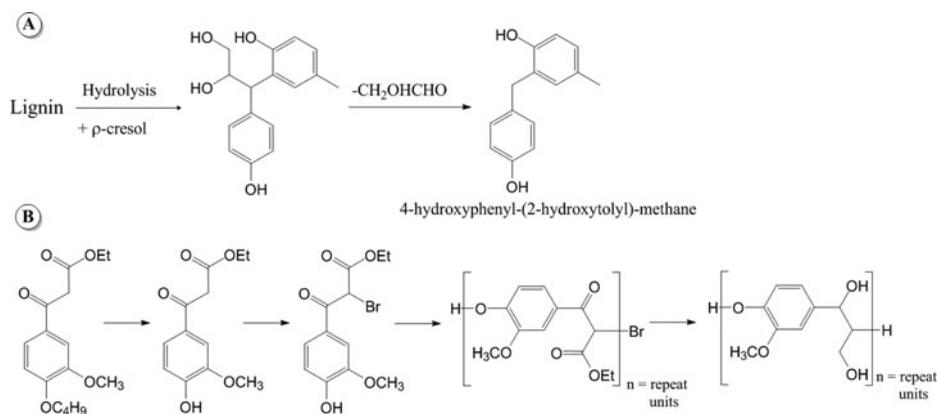
Figure 14. (A) monomer for the synthesis of polyesters and polyethers. Reproduced from Okuda et al.[176] with permission from IOP Publishing. (B) linear polyetherification of monoaromatic monomer from lignin.

Lignin biological degradation can be achieved by enzymes and mediated by extracellular lignolytic enzymes such as lignin peroxidases, manganese peroxidases, and laccases (Fig. 15).[178] These enzymes oxidize the phenolic compounds and the aryl-ether position of the molecule. The by-products of biodegradation are aromatic lignin monomers such as hydrocinnamic acid and vanillic acid. The size, nonhydrolyzability, heterogeneity, and molecular complexity of lignin are the variables responsible for non-specific biodegradation.[179]

3.1.5 Proteins. Proteins are heteropolymers formed essentially from 20 amino acid monomers ordered in different sequences, to give various polymers with a wide range of chain lengths, from 50 monomer units, for example, insulin, to over 100 000 monomer units, for example, wheat gluten. Their complex structure can be partially destroyed or modified by temperature, pressure, or chemical modification.[24]

The most widely used proteins are from grains (soybean, sunflower), cereal co-products (wheat gluten, maize zein), and animal tissue structures (collagen, keratine, gelatine). Grain proteins are usually blended to improve their water resistance and their applications are as films in food packaging, preservation, and thermopressed objects such as automobile body parts.[181] They can be processed through compression molding, injection molding, and extrusion.[182] Cereal proteins are obtained after extraction of the grain starch and include glutenins (polymeric proteins that provide viscous character) and gliadines (monomeric proteins which confer elastic properties). They are used as film-forming agents.[24,148]

Proteins from animal sources include collagen which is composed of different peptides, mainly glycine, proline, hydroxyproline, and lysine. They are enzymatically degradable[148] and can be obtained from animal waste such as bones and skin (section 2.14). Gelatine is a semicrystalline protein produced from the splitting and depolymerization of collagen molecules. It is a high molecular weight polypeptide and commonly it is cross-linked to other substances to improve the thermal and mechanical properties. It is suitable for injection molding but is commonly used for film production. Its creep properties are related to the extent of crosslinking, typically by glutaraldehyde.[183]

Proteins are considered to be ideal templates for biomaterials as temporary replacement implants due to their ease of processability, adhesion to various substrates and surface active properties. Their main application is in the biomedical area, food packaging,[182] and for
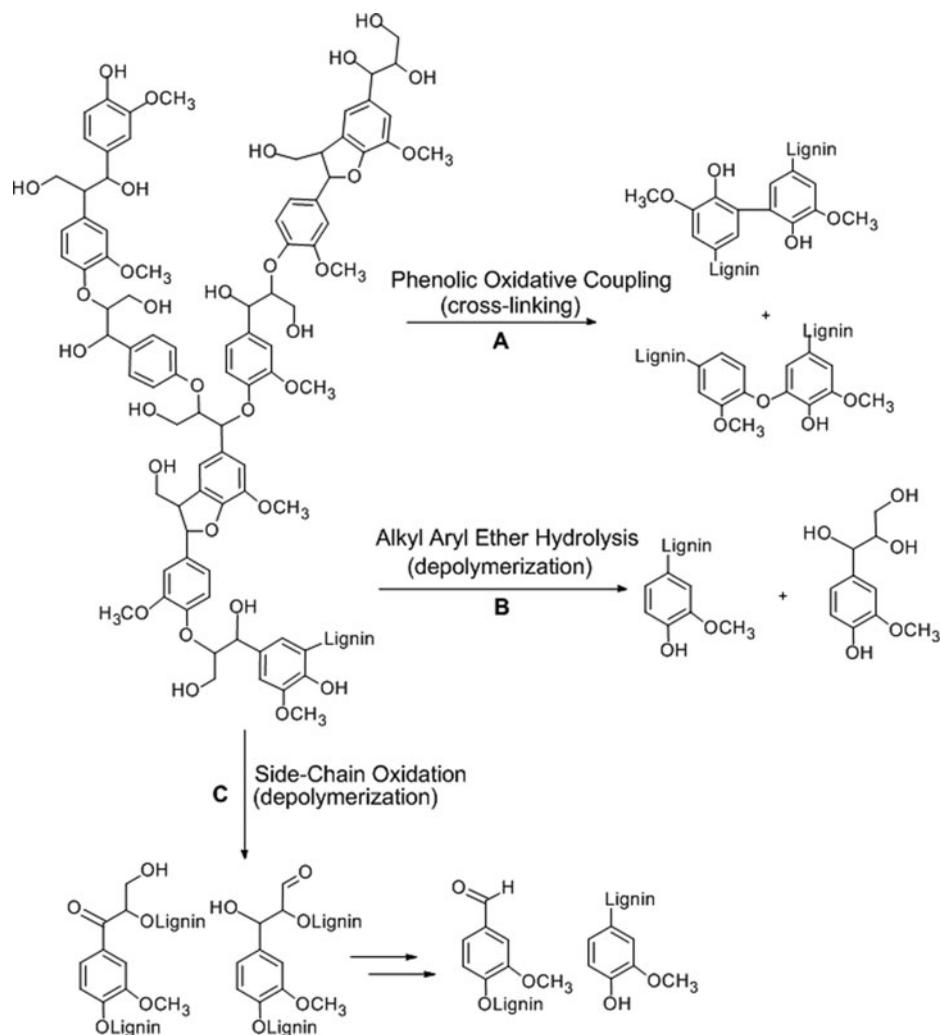
Figure 15. Oxidative pathways for lignin biodegradation.

molded products or edible films.[184] They are biodegraded via amide hydrolysis reactions by enzymes such as proteases.[35,185]

3.1.6 Plant Oils. Fatty acids and terpenes perhaps provide the most familiar routes to polymers derived from biomass. Henry Ford said of waste products from farming "Now we've got all this useless waste, let's see if we can do something with it," and in 1932–1933, the Ford Motor Company spent over a million dollars on soybean research, equivalent to 16.5 million dollars today using the consumer price index.[186]

Tryglycerides are triesters of glycerol with long-chain fatty acids with variations in the fatty acid compositions (Fig. 16). They can be obtained from several food wastes such as peanut husks, potato waste, mango seed, citrus peels, coffee waste, pumpkin seed, and banana peel (Tables 1 and 2). The difference in structure depends on plant, crop, season, and growing conditions of the plant. The stereochemistry of the double bonds of the fatty acid chains, the degree of unsaturation and the length of fatty acids are the parameters that affect the physical and chemical properties.[18]
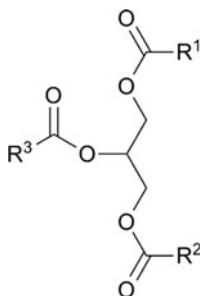
Figure 16. Basic structure of natural triglycerides, where R^1, R^2 and R^3 are fatty acids aliphatic chains.

Fatty acids are classified depending on their iodine value.[188] Values higher than 130 corresponds to drying oils, between 90 and 130 are semi-drying oils, and values lower than 90 are for non-drying oils. Drying oils are mainly used in industry for their high capability for autoxidation, peroxide formation and subsequent radical polymerization.[182]

Two sites in the triglyceride structure are suitable for a chemical modification; (i) ester moieties which can be hydrolyzed or transesterified and then subjected to further modification, (ii) reactive functions along the aliphatic chains, most frequently at the $C = C$ unsaturated site and OH groups.

These are mainly converted into hydroxyls groups, which can be directly transformed into other reactive moieties, such as polymerizable acrylics or styrenic functions.[143]
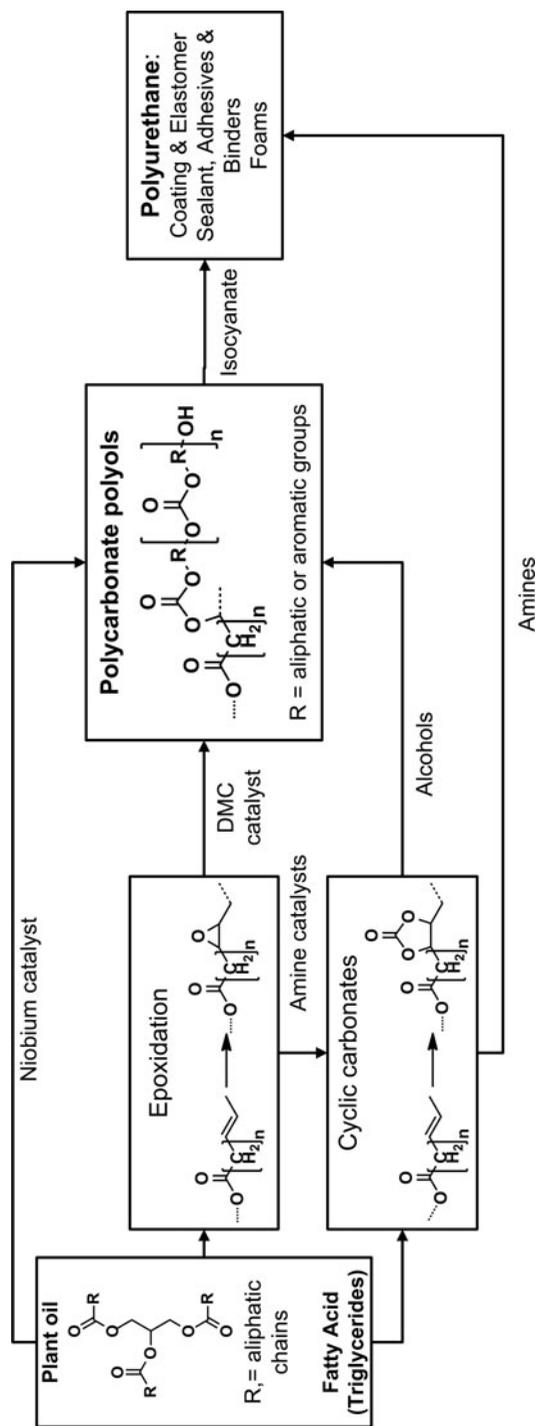
Epoxidized plant oils and fatty acids have been used widely for the production of epoxy resins, as plasticizers, stabilizers for PVC, components in painting and coating formulations, and for the production of thermosetting biomaterials. On an industrial scale, the unsaturated fatty compounds are converted into epoxidized plant oils by the *in situ* performic acid procedure.[182] Their incorporation into biopolymers increases flexibility, lowers the melting point, and increases hydrophobicity. Their use for the preparation of several biopolymers, as polyols for polyurethanes production, has been already reviewed.[26,189,190] General synthetic routes for the production of biopolymers from oils are explained in Fig. 17.

In the case of citrus peel oil, the major chemical compound is limonene which is an optically active monocyclic hydrocarbon terpene, made up of two isoprene units. It is a non-conjugated diolefin with internal and external double bonds.

The reaction mechanism of terpenes like d-limonene with solid acids catalysts initiates with an isomerisation on the acid sites followed by the dehydrogenation of the resultant intermediates. The use of a noble metal as catalyst enhances the dehydrogenation activity of the reaction.[191]

The direct hydrogenation of limonene produces ρ-menthene and ρ-menthane. The further appearance of terpinolene, α-terpinene, and γ-terpinene indicates that an isomerization process precedes hydrogenation, while simultaneously a dehydrogenation takes place generating ρ-cymene and dimethylstyrene. Limonene and terpinolene are coupled by a fast isomerization reaction forming ρ-menthene, α-terpinene and γ-terpinene, while ρ-cymene is formed from γ-terpinene via dehydrogenation process and stabilized by π-electron delocalization through resonance. The further hydrogenation of ρ-menthene will form ρ-menthane while the dehydrogenation of ρ-cymene will form dimethylstyrene. (Fig. 18).[191,192]

Most research is focused on the conversion of D-limonene into the intermediate ρ-cymene[193–196] as it can be used for the production of fragrances, herbicides, pharmaceuticals,

Figure 17. Synthetic routes for biopolymer production from plant oils. Modified from Petrovic et al.[190] with permission from Taylor & Francis.

Figure 18. Scheme of the hydrogenation, isomerisation and dehydrogenation of d-limonene over Pd catalyst.

and heat transfer media. But the further dehydrogenation produces dimethylstyrene which has a similar structure to styrene and hence can be polymerized or copolymerized.

Poly-dimethylstyrene is obtained through low temperature cationic polymerization by use of a Lewis acid catalyst, mainly boron triflouride etherate. The reaction takes place at $-78°C$ under nitrogen atmosphere during one hour using as solvent a liquid saturated aliphatic or aromatic hydrocarbon which remains in liquid form at the reaction temperature, toluene being the solvent which gives the best results.[197] Afterwards, the polymer is precipitated with the use of pre-cooled methanol.[198] The polymer obtained presents a high degree of crystallinity and melting point around 200°C.[199,200] Copolymers with poly-DMS have been achieved using *p*-isopropyl-α-methylstyrene,[201] butadiene,[202] maleic anhydride,[203] and thermoplastic compositions such as acrylonitrile and maleic acid derivatives.[204]

3.1.7 Sugars. As explained previously, starch and lignin can be decomposed into sugars which can be further utilized for the production of furfural derivatives which are used for the production of furans.

The most common furfural derivatives are, in order of importance, 5-hydroxy-methylfurfural (5-HMF); 2,5-furan-dicarboxylic acid (2,5-FDCA); 2,5-dimethylfuran (2,5-DMF); 2,5-diformylfuran (2,5-DFF) and 2,5-bis(hydroxymethyl)-furan (2,5-BHF). They are mainly produced from the acid catalyzed dehydration of hexoses such as glucose and fructose and polysaccharides such as xylan, sucrose, starch, cellulose, and lignocelluloses, as mentioned in sections 3.1.1 and 3.1.2. Under acidic conditions the pentosan is initially converted to a pentose, followed by its dehydration and cyclization to furfural (Fig. 19).

The synthesis of 2,5-diformylfuran, 2,5-furandicarboxyl acid, and 2,5-bis(hydrox-ymethyl)-furan come from the further catalytic transformation of the 5-hydroxym-

Figure 19. Synthesis of furfural.

Figure 20. Main structures of furfural derivatives.

ethylfurfural (Figs. 20 and 21). Several authors have reviewed the possible chemical modification that can be applied to 5-HMF.[206–208]
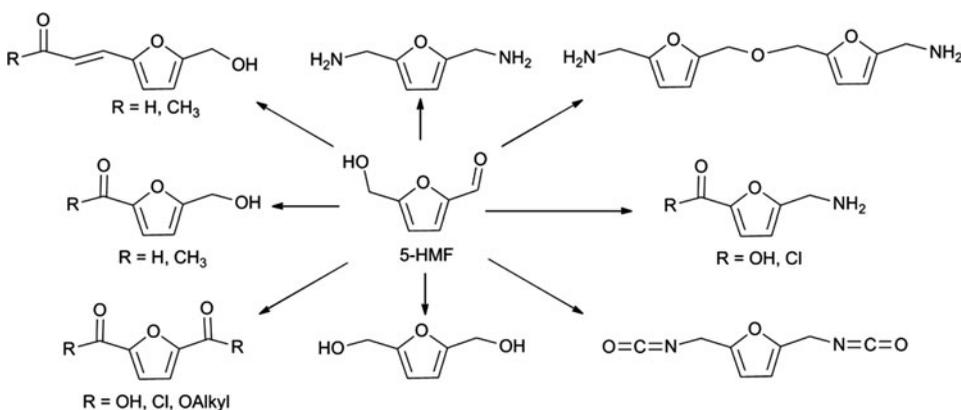
These furfurals and their derivatives can be used as monomers for the production of polymeric materials such as polyesters, polyamides and polyurethanes. It is also possible to obtain biopolymers such as Kevlar-like polyamides, furan-based polyconjugated polymers and they are used as replacements for terephthalic acid.[207]

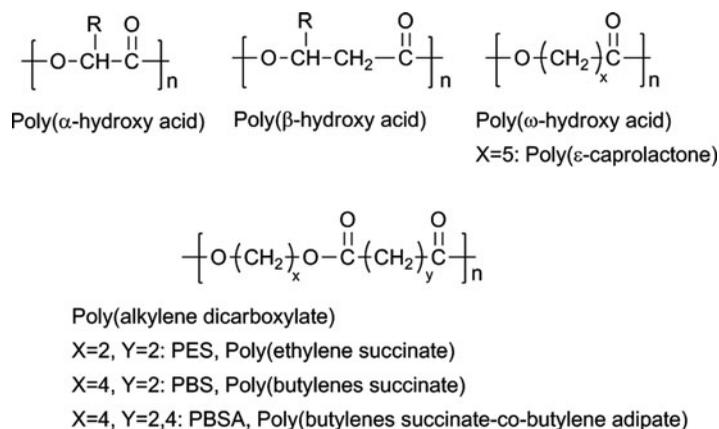### 3.2 Industrial Biotechnology (White Biotechnology)

White biotechnology is a term used for the conversion of renewable resources into new compounds by combined fermentation and enzymatic processes. Applied to the area of polymers, it includes polymers that can be produced in fermentation processes or by chemical polymerization using substrates generated by a fermentation process. The most well-known examples are the aliphatic polyesters PHA and PLA.

Aliphatic polyesters are divided in two main groups according to their bonding mode of the constituent monomers (Fig. 22). One group is the poly(alkylene dicarboxylate)s which are synthesized by polycondensation reactions of diols (HO-R-OH) and dicarboxylic acids (HOOC-R-COOH). The second group contains the polyhydroxyalkanoates which are formed by repeating units of hydroxy acids (HO-R-COOH). The polyhydroxyalkanoates are divided into α, β, and ω-hydroxyacids according to the position of the OH group with respect to the COOH end group.

Aliphatic polyesters are categorized as biodegradable substances because of their potentially hydrolyzable ester bonds but being biodegradable does not necessarily imply that they are bio-based polymers. Only poly(α-hydroxy acid) and poly(β-hydroxy acid)s are derived from agro-resources while the rest are petroleum-based.[209]

Figure 21. Monomers derived from 5-Hydroxymethylfurfuran.

Poly(α-hydroxy acid)   Poly(β-hydroxy acid)   Poly(ω-hydroxy acid)

X=5: Poly(ε-caprolactone)

Poly(alkylene dicarboxylate)

X=2, Y=2: PES, Poly(ethylene succinate)

X=4, Y=2: PBS, Poly(butylenes succinate)

X=4, Y=2,4: PBSA, Poly(butylenes succinate-co-butylene adipate)

Figure 22. Structures of Aliphatic Polyesteres. n = polymer degree.

PLA is produced by the chemical condensation of lactic acid obtained by fermentation while PHA comes from bacterial processes. Both biopolymers use carbohydrate feedstocks for their production. These can be obtained from the food wastes reviewed in section 2, notably peanut husk, coffee waste, banana peel, avocado seed, carrot waste, and oat husks. For this reason only these biopolymers are discussed here.

3.2.1 Poly(β-hydroxyalkanoate)s - PHAs. Poly(β-hydroxyalkanoate)s (PHAs) are aliphatic polyesters synthesized by different types of bacterial fermentation: microbes such as *Bacillus megaterium, Alcaligens eutrophus, Alcaligens eutrophus* and natural isolates of *Actinobacillus, Azotobacter, Agrobacterium, Rhodobacter*, and *Sphaerotilius* accumulate them as osmotically inert carbon and energy storage compounds in the form of granules.[210] The properties of PHA depend on their structure (Table 32). The simplest PHA is a relatively hard and brittle material with a melting point slightly below the thermal decomposition temperature.[211] With pendent groups C_6 and longer (eg Nodax[TM] produced by Procter & Gamble) they are much easier to process than the shorter chain PHA and are similar to propylene properties.[212] Higher molecular weight monomers are

Table 32
PHAs structures

PHB	$R = CH_3$
PHBV	$R = CH_3ORCH_2CH_3$
mclPHA	$R = (CH_2)_{n = 0-12} CH_3$

typically rubber-like materials with an amorphous soft/sticky consistency.[213] The choice of polymerase, host, feedstock, and conditions produces different PHA ranges during the bacterial fermentation with diverse physical properties. PHA copolymer properties vary according to the comonomer unit structure, content, and distribution on the polymer chains.

The biodegradation of these polymers into water-soluble oligomers and monomers occurs by lipases or by extracellular PHA depolymerase excreted from a variety of microorganisms found in the environment which make use of the resulting products as nutrients.[214] As they are biodegradable, their applications have tended to be focused on medical applications, disposable items, and because of their impermeability to water and air, they are considered for the production of bottles, films, and fibers.[215]

3.2.2 Poly(β-hydroxybutyrate), PHB. Poly(β-hydroxybutyrate) (PHB) in its pure form is a brittle thermoplastic polymer[216] with narrow processability windows.[211] Commercially, it is mixed with other hydroxyalkanoate units to improve the properties, such as the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) produced by Monsanto, known industrially as Biopol[TM] and Nodax[TM] PHA copolymers by Procter and Gamble.

3.2.3 Poly(hydroxybutyrate-co-hydroxyvalerate), PHBV. PHBV is produced by a microbial fermentation process of glucose and propionic acid. The synthetic pathway for poly(hydroxybutyrate-co-hydroxyvalerate) [P(HB-co-HV)] is achieved by coupling the PHB biosynthesis with the pathway generating 3-propionyl-CoA via threonine deaminase and pyruvate decarboxylase. The synthesis is shown in Fig. 23.

PHBV is a crystalline polymer with thermal properties similar to polypropylene. The disadvantages are: (i) the thermal degradation which occurs almost at the melting temperature, (ii) low impact resistance at room temperature, (iii) high crystallinity due to the stereo-regularity of the isotactic chain configuration, and (iv) high glass transition temperature.[217]

The high crystallinity results in a hard and brittle material, which combined with other disadvantages limits the range of applications.

By regulating the content of 3HV (hydroxyvalerate) units added to the feedstock, the impact strength, flexural modulus, melting point, and extent of crystallization can be controlled. The addition of 3HV decreases the crystallinity and reduces the melting point of the original PHB. Unfortunately the use of 3HV units is limited in efficacy because they can be easily included in the crystal lattice of 3-hydroxybutyrate (3HB).[212]

3.2.4 Poly(β-hydroxyalkanoate) Copolymers. This is a copolymer composed of 3HB units and a medium chain length 3-hydroxyalkanoate (mcl-3HA) unit. The chain length of the comonomer should be larger than the 3HV used in the PHBV so that the copolymer can have side groups with 3 or more carbon units. The copolymer grade depends on the (mcl-3HA) unit selected, its molecular weight, the fraction in the copolymer structure and the side group chain length. Some examples of 3-hydroxyalkanoate are: 3HHX (3-hydroxyhexanoate), 3HO (3-hydroxyoctanoate) and 3HD (3-hydroxydecanoate). The addition of mcl-3HA regulates the melting temperature and crystallinity, resulting in high toughness and ductility. As long as the side group has more than three carbons, the improvements to the physical properties are independent of the mcl-3HA size.[212] Biodegradation can take place under aerobic conditions to produce carbon dioxide but under anaerobic environments there is a danger that methane might be liberated.[218]
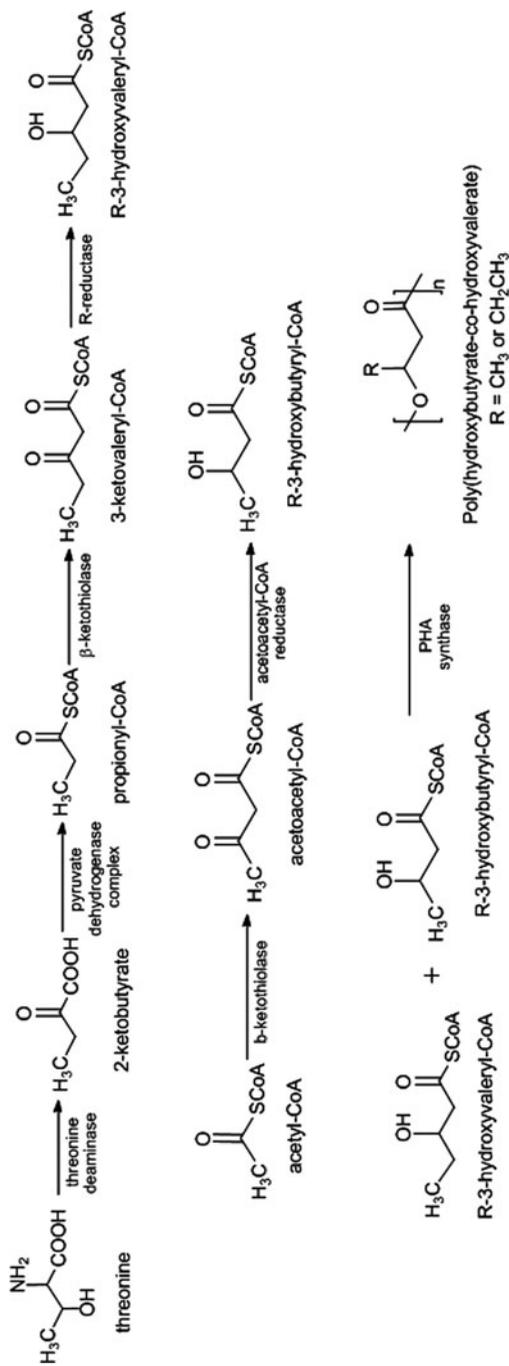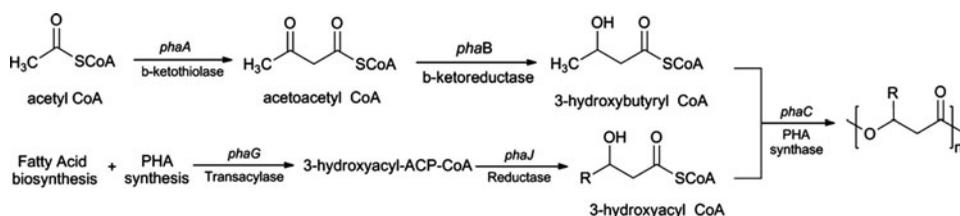
Figure 23. PHBV pathway synthesis.

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Figure 24. Biosynthesis of PHA copolymers.

The copolymer biosynthesis route is explained in Fig. 24. It involves parallel enzymatic reactions for the production of each co-monomer, and both reactions start with a fatty acid biosynthesis followed by its acid oxidation. These reactions use microorganisms whose partial genomic DNA sequence showed putative PHA synthase genes (open reading frames, ORFs);[219] in Fig. 24 they are mentioned as pha genes.

3.2.5 Polylactic Acid - PLA (Poly(α-hydroxy acid)). PLA is an aliphatic polyester synthesized by the condensation polymerization or ring opening polymerization of the D- or L-lactic acid as the monomer (2-hydroxy propionic acid). Lactic acid chains are produced by the microbial fermentation of starch from renewable sources including food wastes.[220]

The most commonly used carbon sources for PLA production are sugar–containing materials, cassava starch, lignocellulose/hemicellulose hydrolysates, cotton seed hulls, Jerusalem artichokes, corn cobs, corn stalks, beet molasses, wheat bran, rye flour, sweet sorghum, sugarcane press mud, cassava, barley starch, cellulose, carrot processing waste,

Table 33

Renewable sources and microorganisms used for PLA production.[223]

Substrate	Microorganism	Lactic acid yield / g/g
Wheat and rice bran	*Lactobacillus sp.*	1.29
Corn cob	*Rhizopus sp.MK-96–1196*	0.90
Pretreated wood	*Lactobacillus delbrueckii*	0.48–0.62
Cellulose	*Lactobacillus coryniformis ssp. Torquens*	0.89
Barley	*Lactobacillus caseiNRRLB-441*	0.87–0.98
Cassava bagasse	*L. delbrueckii NCIM 2025*	
L casei	0.9–0.98	
Wheat starch	*Lactococcus lactis ssp. lactis ATCC 19435*	0.77–1
Whole wheat	*Lactococcus lactis*	
Lactobacillus delbrueckii	0.93–0.95	
Potato starch	*Rhizopus oryzae*	
R. arrhizuso	0.87–0.97	
Corn, rice, wheat starches	*Lactobacillus amylovorous ATCC 33620*	< 0.70
Corn starch	*L. amylovorous NRRL B-4542*	0.935

molasses spent wash, corn fiber hydrolysates, and potato starch. The choice of the feedstock depends on the purity, availability, and price.[221] It is produced industrially by the bacterial fermentation of carbohydrates at pHs of 5.4 to 6.4 in the temperature range 38–42°C, at low oxygen concentration and in the presence of microorganisms through solvent-free polymerization.[222] The microbal fermentation can be carried out by bacterial species such as *Lactobacillu, Streptococcues, Leuconostoc,* and *Enterococcues* or fungal strains such as *Mucor, Monilina, and Rhizopus* (Table 33).[221] There are three ways to produce lactic acid polymerization: (i) direct condensation polymerization based on monomer esterification, (ii) direct polycondensation in an azeotropic solution using a catalyst and (iii) polymerization through lactide formation without the use of solvent. The main advantage of this biopolymer is the minimum emission of CO_2 during production.[222]

The most common polymerization method is the ring-opening polymerization of lactide (the cyclic lactic acid dimer). A low molecular weight PLA (M.Wt. 1000-5000) is formed and then depolymerized through an internal transesterification to the cyclic dimers that can have three different stereoforms (Fig. 25). Catalytic ring opening polymerization is then performed to give a high molecular weight PLA or PDLA (when a mixture of L-lactic and D-lactic acid is used).

PLA is a hydrophobic polymer, and a biocompatible thermoplastic with a relatively high melting point (170°C). It is a completely biodegradable biopolymer with high tensile strength (70 MPa) which can be recycled from 7 to 10 times.[224] PLA is a crystalline polymer while PDLA is an amorphous polymer, but the degree of crystallinity can be controlled by the ratio of D to L enantiomers used. Table 34 indicates the general properties of PLA: the physical properties and biodegradability can be regulated by racemisation of the monomer or using a co-monomer component of hydroxyl acids.[217]

PLA is classified as a hydro-biodegradable polymer because it has to pass through a high temperature chemical hydrolysis for its degradation. Moisture splits the macromolecules into smaller units which are consumed by microbes and converted to carbon dioxide and water. It can also be degraded by depolymerization in alkaline conditions to the cyclic dimer.

From a chemical point of view, the polymer degradation occurs when an electrophilic attack to the hydroxyl end-group on the second carbonyl group provokes a ring formation

Table 34
PLA characteristic properties.[37,223]

Physical properties	
Melt flow rate (g/10 min)	4.3–2.4
Density /kg m^{-3}	1250
Haze	2.2
Yellowness index	20–60
Mechanical properties	
Tensile strength at yield /MPa	53
Melt flow rate (g/10min)	4.3-2.4
Impact strength index /kJ/m^2	2.6
Elongation at yield (%)	10–100
Flexural modulus /MPa	350–450
Thermal properties	
Heat Distortion Temperature /°C	135
Melting point /°C	150-170
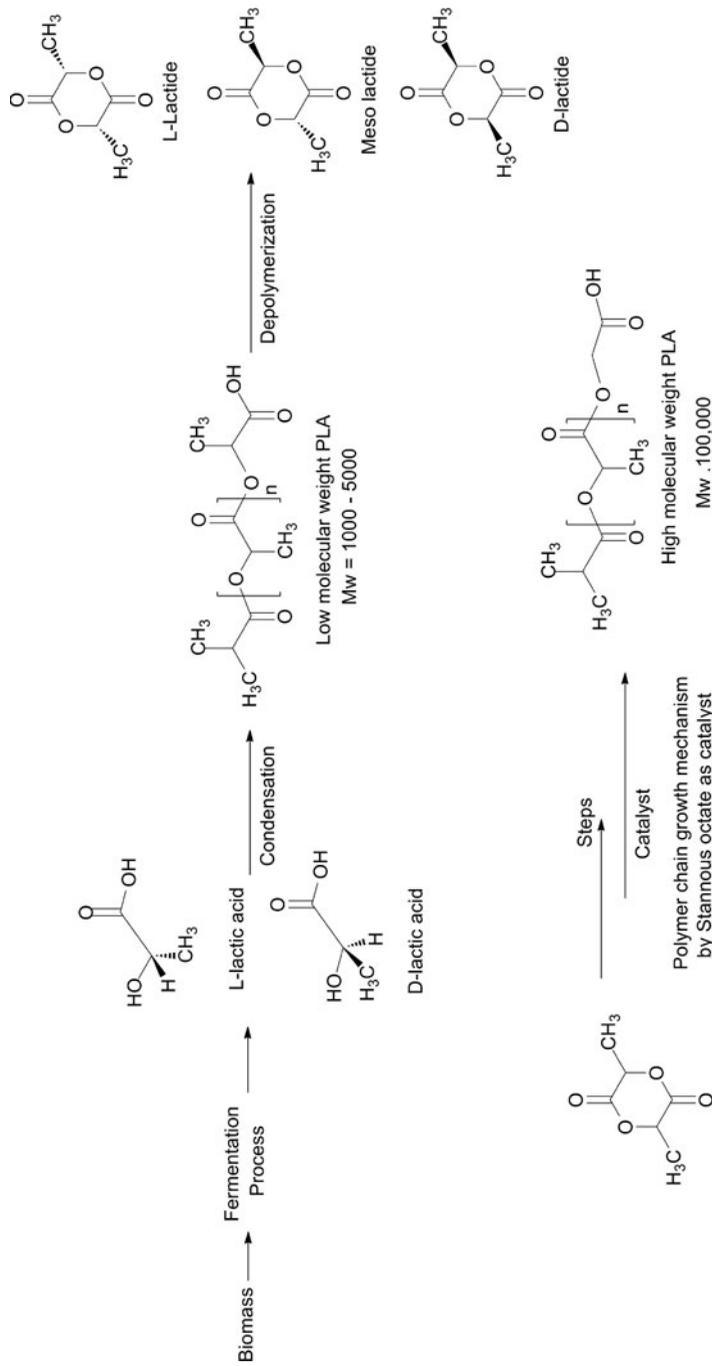
Figure 25. PLA polymerization.

675

Protoporphyrin IX
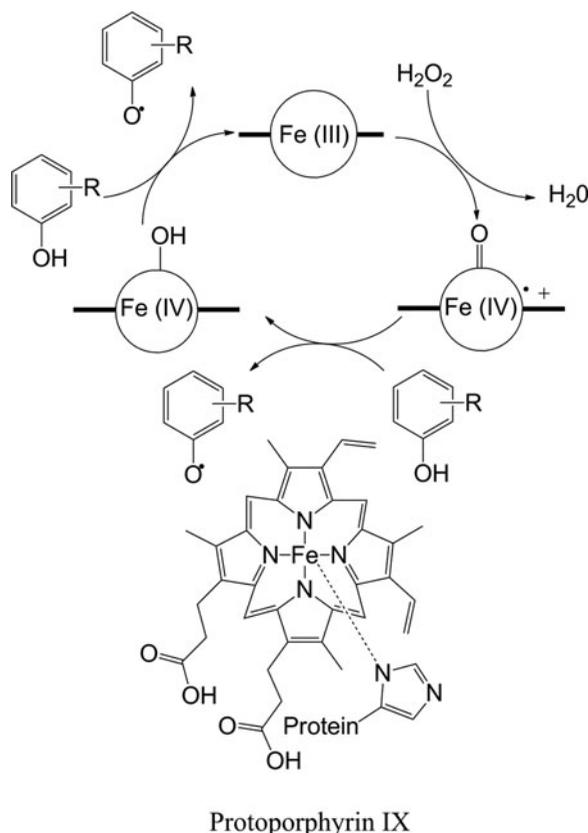
Figure 26. HRP catalytic reaction.

and the polymer is shortened by the hydrolysis of the ester link from the resulting lactide. Subsequently the hydrolysis of the ester group from the free lactide releases two molecules of lactic acid.[223]

3.2.6 Enzymatic Oxidative Polymerization. This type of polymerization takes place with enzymatic catalysis using oxido-reductase enzymes which catalyze the decomposition of hydrogen peroxide at the expense of aromatic proton donors letting the polymerization take place. They contain low-valent metals, as catalytic centers like

- Iron (III) - (HRP – horse radish peroxidise)
- Copper (I) - (Lacasse)
- Manganese (II) - (Manganese peroxide)

These enzymes are known for the production of polyphenols, polyanilines, and vinyl polymers.[225] The most common enzyme used for polymerization processes is the HRP. This enzyme contains porphyrin-type structure which takes hydrogen peroxide as oxidant. The polymerization reaction takes place at room temperature in aqueous solutions producing oligomeric compounds which usually have low solubility toward the solvent causing polymers of low molecular weight. The catalyst reaction is shown in Fig. 26.

Several studies are based on the enzymatic oxidative polymerization of phenol using horseradish peroxide[227–230] as catalyst. One example is Oguchi's work[227] which focuses on the study of the polyphenol solubility, composition, and molecular weight and the effects of
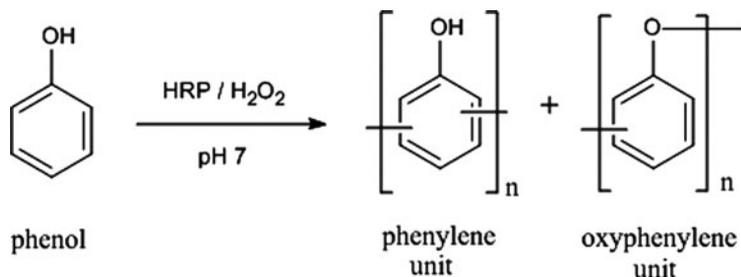
Figure 27. Polymer structure of polyphenol.

modifying the reaction conditions. The polymerization reaction is initiated by the addition of hydrogen peroxide as an oxidizing agent causing the formation and precipitation of a fine powder collected by centrifugation. Oguchi's results indicated that the polyphenol obtained through enzymatic polymerization consisted of two different unit structures: phenylenene and oxyphenylene (Fig. 27).

Research in the polymerization of phenol derivatives has also used HRP[231–235] and lacasse[236–238] as catalytic enzymes. Of interest for this review is the polymerization of caffeic acid, which is found in the phenolic compounds of potato waste. Xu's work[235] emphasizes in the biocatalyst in-situ polymerization of caffeic acid on a functionalized gold surface and its structural comparison with the same polymer obtained by solution enzymatic polymerization. Both reactions were accomplished using horseradish peroxise (HRP) enzyme as catalyst.

Another useful example is the enzymatic oxidative polymerization of chlorogenic acid (Fig. 28), also found in potato waste. The initial step would be the formation of an o-quinone by enzymatic oxidation. The subsequent steps rely in non-enzymatic reactions. A second step is the conversion of half of the quinone into hydroxyquinone and regeneration of chlorogenic acid from the other half. At the end, polymerization of hydroxyquinone takes place.[239]

3.3 Transgenic Plants

The scope for genetic modification to food crops in order to increase yield, resist predators or confer resistance to arid conditions, extends also to plants intended to yield raw materials that replace those derived from mineral oil. Of particular interest is the potential to exploit land which is presently unusable and to resist desertification driven by climate change.[240–242] More specifically, this technology may facilitate and extend the synthesis of polymers in agricultural crops. Modification by using genetic engineering techniques to introduce microbial genes which encode the biosynthetic conversion of specific substances in the
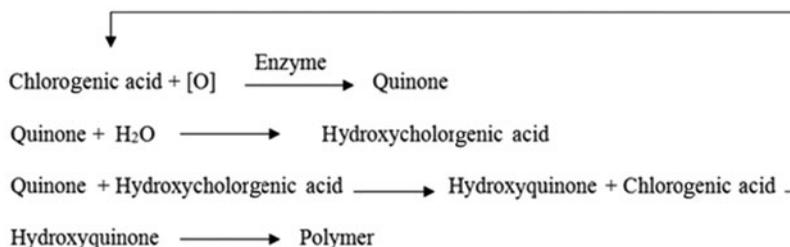

Figure 28. Reactions which takes place in chlorogenic acid enzymatic oxidative polymerization.

plant, followed by polymer recovery through extraction with organic solvents is one route. The goal is to obtain engineered crops that would obtain biomass-derived polymers with better properties and potentially on large scale production compared to those obtained from mineral oil sources.[243–245] Due to the natural decomposition of organic tissues such as those present in plants, it is a priority also to consider the time between the harvesting season and the extraction of the polymer. Because of this, the production of the polymer in seeds, which usually can be stored for a long time without changing their biochemical characteristics, is a potentially interesting solution.

The development of this technology has three major disadvantages, the current high cost of industrial production, the greenhouse gas emission from the overall production process[246] and the lack of public acceptance for genetically modified plants. The overall cost of discovery, research and development, breeding, production, admission, and regulatory clearance for each country can, under present circumstances be prohibitive.[247] Currently, sugar beet, sugar cane, certain potato varieties, and fiber crops are being used for the industrial production of crops.[140]

4. Fibers and Other Reinforcements

This review focuses on food wastes that can be used for the production of hydrophobic polymers but the mechanical properties of such polymers can be improved by fiber reinforcement to produce polymer matrix composites[248,249] and short staple fibers for this purpose can also be derived from biomass and potentially from food wastes. Already hemp, jute, ramie, and flax fibers are appearing in fiber reinforced polymers[250,251] and have even been used in the bodywork of sports cars: the Lotus Eco Elise has body panels and trim made of hemp, eco wool, and sisal.[252] As another example, rice-hull is being used as a filler material for polymer composites.[253] Rice hulls were identified as a source of silicon carbide in 1975 and so contribute to the production of ceramic materials as well as polymer composites.[254] They have been used to generate materials with polyvinyl chloride (PVC),[255] PLA,[256] polypropylene (PP),[257] polyethylene (PE),[258] and high density polyethylene (HDPE).[259] Other examples are pineapple and coconut husk used as natural reinforcing fibers.[260–262] Fibers generated from straw waste are also used as reinforcement as well as having many other uses.[263] A general classification of natural fibers and examples of applications is shown in Fig. 29.

Fibers such as sugarcane bagasse, oat hulls, corn husks, rice, and wheat straw can be used for the production of furfural resins. The furanic monomers are obtained directly from
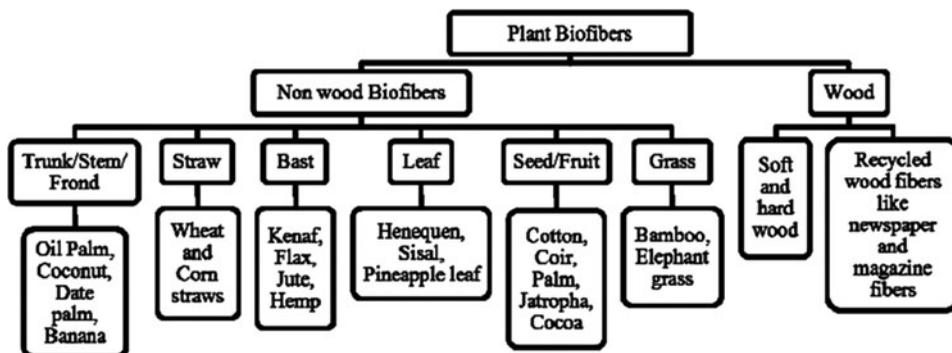
Figure 29. Classification of natural fibres. Reproduced from Khalil et al.[251] with permission from Elsevier.

the hemicelluloses found in these agricultural residues by an acid-catalyzed hydrolysis of pentosans followed by the dehydration and cyclization of the pentoses. Its industrial utilization started in 1960 when the Quaker Oats Company (USA) introduced furan resins as binders in the foundry industry and since then it has been used in combination with formaldehyde, urea, phenol, and casein for decades.[264] Further discussion of furans and their derivatives is given in section 3.1.7.

Moving outside the area of food wastes but keeping the theme of zero embodied fossil carbon materials, another source of reinforcement is the use of smectite clays to produce polymer-clay nanocomposites. These were first invented by Toyota Motor Corporation[265] and interest has expanded considerably since.[266,267] An advantage of the use of short fiber or smectite clay reinforcement is that it does not restrict the fabrication routes for thermoplastic biomass polymers so that extrusion and injection molding, for example, can still be used but it enhances elastic modulus and may help to ameliorate seasonal or annual variations in products due to prevailing growth conditions.

5. Biodegradation of Polymers from Food Waste

Biodegradation of polymers can be defined as the macromolecular degradation of a solid polymeric material into by-products such as water, carbon dioxide, minerals, oligomers, monomers, or intermediate compounds in a natural environment resulting in the loss of the mechanical, structural, and chemical integrity of the original bulk polymer (based on ref. 268). The biodegradability of a polymer and hence its final product composition depends on the chemical structure of the bulk material. It tends to be less dependent on the raw materials used for the production of the polymer. The pathways by which biodegradation of natural and synthetic polymeric substances can be achieved are: (i) the use of microorganisms which are divided into two groups: fungal digestion under aerobic conditions and bacterial digestion which can be aerobic or anaerobic; (ii) enzymatic degradation, and (iii) non-enzymatic degradation. Comparison of the last two techniques is shown in Table 35.

Hydrolytic degradation realized by enzymes and chemical hydrolysis is shown by the example in Fig. 30.[35] The first reaction (8a) is a biological oxidation, generally performed by enzyme degradation processes. There are three different enzymes that perform this reaction; (i) hydroxylase enzymes which directly incorporate oxygen in the substrate, (ii) oxygenase enzymes that insert the whole oxygen molecule, and (iii) oxidase enzymes that use the oxygen molecule as a hydrogen acceptor producing H_2O and a H_2O_2. The second reaction (8b) is the hydrolysis of the peptide bond followed by the hydrolysis of the ester bond (8c).
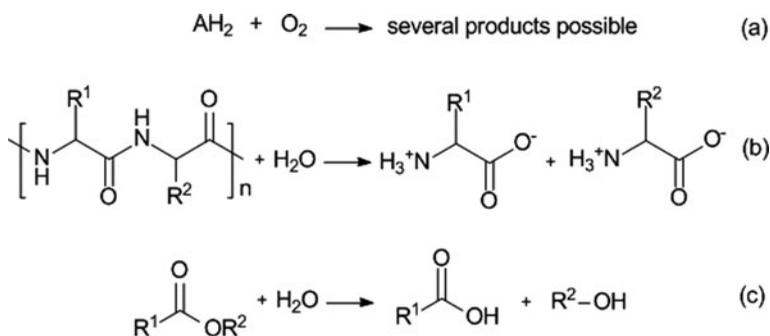
**Figure 30.** General biological hydrolytic degradation by enzymes.

Table 35
Differences between enzymatic and non-enzymatic degradation.[214]

Enzymatic degradation	Non-enzymatic
Based on biological oxidation and biological hydrolysis.	Based on chemical hydrolysis and diffusion of reagents into the polymer.
Surface degradation	Bulk degradation
Enzymes cannot penetrate polymer systems.	Depth degradation by water penetrating the complete polymer structure.
Enzymes first degrade amorphous and less ordered regions and subsequently crystalline regions.	Crystallinity, crosslinking, and morphological properties of the polymer affect the diffusion.
Major molecular weight changes do not occur.	Random scission in the hydrolytic chain produce a reduction in the molecular weight causing decline of mechanical properties.
The polymer on the surface is degraded by enzymes and the low molecular weight degradation products are removed by solubilization in the aqueous medium.	Morphological fragmentation of the polymer only occurs at the last stage of the degradation.
It can be endo-type degradation (at random points in the chain) or exo-type degradation (at the ends of the chain)	—

The hydrolytic degradation process can progress via a surface or bulk degradation pathway according to the diffusion-reaction of the degradation process, Fig. 31.

Surface degradation, known as erosion degradation, involves the hydrolytic reaction taking place on the surface of the polymer. In this process the production of oligomers and monomers is faster than the rate of water intrusion into the polymer bulk, provoking a thinning of the polymer without affecting the molecular weight of the polymer bulk. This process follows shrinking unreacted core kinetics[269] so that progress of degradation is predictable making such polymers suitable for use as vehicles for drug delivery.

On the other hand, bulk degradation is caused when the hydrolysis is achieved by the penetration of water into the bulk polymer producing a reduction in the molecular weight of the polymer. Typically, equilibrium exists between the water introduced into the bulk material and the outward diffusion of monomer or oligomer. If this equilibrium is disturbed, an internal autocatalytic degradation process (in the case of aliphatic polyesters made via the carboxyl and hydroxyl end group by-products) may occur. This autocatalysis accelerates the internal degradation compared to that on the surface and can produce a hollowed out structure with a bimodal molecular weight distribution, that is,
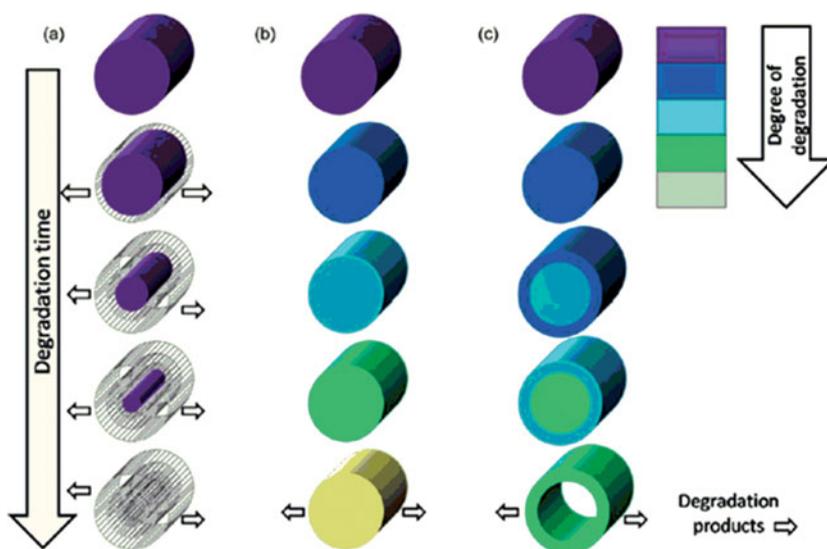
Figure 31. Degradation pathways. a) Surface erosion, b) bulk degradation, c) bulk degradation with autocatalysis. Reproduced from Woodruff et al.[268] with permission from Elsevier (Color figure available online).

with an outer layer with high molecular weight and an internal layer of lower molecular weight.[268]

6. Conclusions

Three factors are likely to displace the polymer and composite materials market towards biomass resources and away from mineral oil feedstock. They are: (i) the upward drift in mineral oil price, (ii) regulatory interventions intended to address climate change, and (iii) consumer preference for "eco-products." This may have an impact on land-use, exacerbating the existing conflict between biofuel and food production. The intelligent redeployment of food waste materials extinguishes this conflict and potentially realigns the agricultural and industrial economic sectors: sectoral integration is sometimes seen as a source of economic stability. If these projections are correct, companies that have positioned themselves with the technology to exploit biomass resources are well placed to take advantage of a plentiful supply of food waste. A clear link between food producers, food processors, and materials producers thus unfolds. At present, bio-polymers are starting to participate in the market as commercial PLA and PHA (Nodax®) are already an accepted part of the plastics industry.

Although there are many agricultural species which yield food production wastes, the raw materials that issue from them are few in number, principally fatty acids and terpenes, sugars, celluloses, starches, lignin, proteins, polyphenols, and fibers. The limited range is however, compensated by the high tonnage of food wastes available annually worldwide from the food-processing industry.

The main sources which could be deployed in biopolymer production are potato waste, mango seed, citrus peel, coffee waste, straw, sugar bagasse, pumpkin seed, banana peel, avocado seed, corn stover, carrot waste, and peanut husk. Grape waste is also a candidate

but its waste products are reasonably well integrated into the economy already. These types of food waste are the most viable and they are produced, processed and commonly used in the majority of countries in the world, even though the quantity varies according to the region, Human Development Index of the country, and consumer social behavior.

There are three strategic pathways for biopolymer production: (i) chemical derivation from biomass, (ii) biochemical modification of the components, or (iii) polymer precursor production in genetically modified transgenic plants. All provide a polymer product with added value. Furthermore, the characteristics of the bio-polymers thus obtained could be improved by using reinforcements themselves sourced from natural resources such as plant fibers and smectite clays.

7. Abbreviations

1P	Proven resources from oil
BHF	Bis(hydroxymethyl)-furan
DFF	Diformylfuran
DM	Dry matter
DMF	Dimethylfuran
FAO	Food and Agricultural Organization of the United Nations
FDCA	Furan-dicarboxylic acid
HA	Hydroxyalkanoate
HD	Hydroxydecanoate
HDPE	High density polyethylene
HHH	Hydroxyhexanoate
HMF	Hydrocymethylfurfural
HO	Hydroxyoctanoate
HV	Hydroxyvalerate
IEA	International Energy Agency
INAO	Institut National des Appellations d'Origine
mcl	Medium chain length
NFE	Nitrogen Free Extract
ORF	Open reading frames
PBS	Poly(butylene succinate)
PCL	Polycaprolactone
PE	Polyethylene
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly lactic acid
PP	Polypropylene
PVC	Polyvinyl chloride
RACOD	Rapidly Acidifying Chemical Oxygen Demand
USDA	United States Department of Agriculture

8. Acknowledgments

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