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## Accepted Article

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# Opportunities for the use of Brazilian biomass to produce renewable chemicals and materials

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## REVIEW

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**Abstract:** This review highlights the principal crops of Brazil and how their harvest waste can be used in the chemicals and materials industries. The review covers various plants; with grains, fruits, trees and nuts all being discussed. Native and adopted plants are included and studies on using these plants as a source of chemicals and materials for industrial applications, polymer synthesis, medicinal use and in chemical research is discussed. The main aim of the review is to highlight the principal Brazilian agricultural resources; such as sugarcane, oranges and soybean, as well as secondary resources, such as andiroba brazil nut, buriti and others, which should be explored further for scientific and technological applications. Furthermore, vegetable oils, carbohydrates (starch, cellulose, hemicellulose, lignocellulose and pectin), flavones and essential oils will be described as well as their potential applications.

## 1. Introduction

Brazil is the biggest country in South America and the fifth biggest nation in the world, covering an area of 8.5 million square kilometers. It is divided into five regions (Center-West, Northeast, North, Southeast and South) with 26 states and one federal district (Figure 1).<sup>[1,2]</sup> The equator passes through the North region, so Brazil is considered to be a tropical country. However, many different climates are seen throughout Brazil due to its large size. These include: entirely tropical wet conditions in the north region, tropical wet and dry weather in the center-west, northeast and southeast, a semiarid region (Caatinga) in the northeast and humid subtropical conditions in the south.<sup>[2]</sup>

Furthermore, the country has six biomes; each with a different type of vegetation. The first biome, Amazonia, is the largest tropical forest in the world and occupies 49% of Brazilian territory. It is situated in the north region and contains a massive quantity of vegetation (1.5 million species). In addition, the Amazon river, the largest river in the world, is found in this region. The Atlantic forest (second biome) occupies 13% of Brazilian territory and is located along the Atlantic coast. Sadly, many native plants and animals in this biome are endangered, due to human activity. The Caatinga (third biome) is a semiarid desert territory (the xeric shrublands) in the northeast region, occupying 10% of Brazilian territory. Due to drought, this region is not good for growing crops and has a low abundance of native plants. Only some shrubs and cactus can grow in this region. The Pampa grassland (fourth biome) is found only in the south region and occupies 2% of the country. This biome receives a large amount of rain in the summer season, experiences negative temperatures in the winter and supports vegetation such as grass, bushes and herbs. The fifth biome, which also occupies 2% of Brazilian territory is the Pantanal, which is a swamp with mangrove vegetation. It is not possible to grow agricultural plants here and the area is mostly used for tourism and cattle farming. The sixth biome (and the second largest) in Brazil is the Cerrado (covering 24% of the country) which is a

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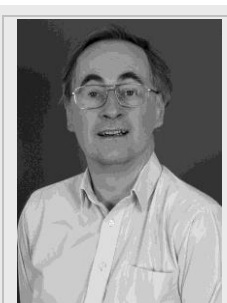
Katie Lamb graduated with a Chemistry degree at the University of York in 2013. In 2017, she obtained her Ph.D. in Green Chemistry at the same institution, researching alternative, novel and sustainable Carbon Dioxide Utilization (CDU) and Carbon Capture and Storage (CCS) methodologies. Since 2018, she has been working as a Postdoctoral Research Associate at the Green Chemistry Centre of Excellence at the University of York, with research interests in sustainable catalysis, carbon dioxide utilisation and cyclic carbonate synthesis.



Gilbert Bannach graduated in Chemistry at Ponta Grossa State University in 2000 and obtained his Ph.D. degree in Analytical Chemistry in 2006 at São Paulo State University. Since 2009 he has been working in the same institution as professor of Analytical Chemistry at Chemistry Department in School of Science. His research aims to transform renewable chemicals (triglycerides, glycerol, terpenes, and carbohydrates) into new monomers and polymers following Green Chemistry Principles.



Michael North obtained his BSc in chemistry from the University of Durham in 1985 and his D.Phil from Oxford University in 1988. After a two year postdoctoral position at the university of Nottingham, he held organic chemistry positions at the Universities of Wales, London and Newcastle. In 2013 he was appointed to a chair in Green Chemistry at the University of York. His research is focussed on developing chemistry for a circular economy including carbon dioxide utilisation; sustainable solvent development and synthesis of biomass derived polymers.



vast tropical savanna with more than 10,000 species of plants, such as various varieties of palm trees, flowers, herbs, fruit trees, and undergrowth vegetation. It is considered the most fruitful region for agribusiness in Brazil, as it is possible to harvest so many different species of plants.<sup>[3-5]</sup>

In summary, as illustrated in Figure 1, Brazil is an enormous country with different biomes and a large quantity of native vegetation, such as fruit trees and nuts. These can be utilized to produce renewable feedstocks and chemicals.

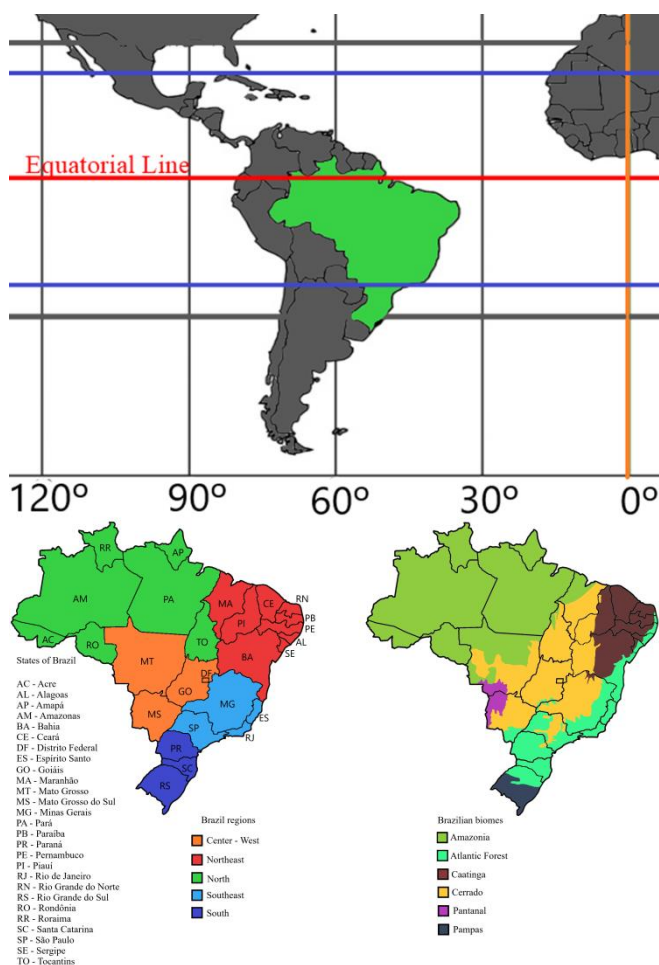


## REVIEW

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Furthermore, Brazil is the largest producer of sugarcane, coffee, and oranges, and it is possible to crop numerous other fruits, grains and nuts.<sup>[6-8]</sup>

This review will describe the main native plants and crops found in Brazil that can be transformed into chemicals and materials and then applied in the chemical industry and in society. Specifically, the review will cover the use of: sugarcane, soybean, cassava and pine nuts as sources of starch and various fruits and nuts. An emphasis is placed on sustainable harvesting and the preservation of native forests whilst obtaining renewable feedstocks.



**Figure 1.** Maps of Brazil showing global position (Top) and Brazilian territories, as classified by regions, states and biomes (Bottom).

## 2. Sugarcane

Since the 16<sup>th</sup> century, sugarcane (*Saccharum officinarum* L.) has been cropped in Brazil.<sup>[9]</sup> Initially, it was mainly grown in the northeast region with a focus on producing sugar (sucrose) from the sugarcane. However, in 1975, the Brazilian Government inaugurated a new policy called “Proalcool”, with the primary aim of increasing ethanol production for use as a greener and renewable replacement for traditional petrochemical fuels.<sup>[10,11]</sup> Consequently, by 2015 85% of commercial vehicles were using ethanol as their fuel.<sup>[11]</sup>

Nowadays, Brazil is the world leader of sugarcane, and therefore sugar, production with a total crop area (in 2016-2017) of 9.1 million hectares<sup>[10]</sup> and a total production of 620 million metric tons in 2018-2019. In addition, Brazil is the second

largest producer of ethanol in the world: 34.4 billion liters were produced in 2019. Sixty percent of this ethanol is produced in the São Paulo State alone (southeast region).<sup>[12]</sup> To produce ethanol, the sugarcane stem is first pressed to remove the broth (which has a sugar content of 24 wt.%). Thereafter, the dried straw (bagasse) is separated and the broth is added into a reactor with a yeast (*Saccharomyces cerevisiae*). This leads to a fermentation process. The yeast is then removed and the fermented broth is distilled to give ethanol and a byproduct called vinasse (*vinhaça*).<sup>[13,14]</sup> The vinasse is a liquid syrup and for each liter of ethanol produced, 12 liters of vinasse are generated. Vinasse contains a large quantity of organic compounds and some inorganic metal cations, such as sodium, potassium, calcium, and magnesium.<sup>[15]</sup> This syrup can become a water pollutant if discarded inappropriately. However, it can be used as a fertilizer to help grow basil,<sup>[16]</sup> sugarcane,<sup>[17]</sup> corn<sup>[18]</sup> and lettuce crops.<sup>[19]</sup>

In addition to ethanol, sugarcane can be harvested to provide many other products, which in turn can be utilized to form a variety of chemicals and materials. These products are described and summarized in the following sections.

### 2.1. Sugarcane Bagasse in composites

Sugarcane bagasse (SB) is a waste product of bioethanol production, which was initially used as a solid fuel in furnaces or in industrial boilers to produce energy. This process, however, is no longer viable, due to the large quantity of sugarcane produced. Recent research into making better use of this material has therefore focused on developing methods to transform this waste into new chemicals and products.

SB has been used as a reinforcing material in polymeric matrices, to form composites with different physical and chemical properties compared to the pure polymeric material. Hence, SB has been used as a filler to improve the tensile properties of a recycled blend of polypropylene maleic anhydride and polypropylene/acetonitrile butadiene rubber.<sup>[20]</sup> A polypropylene (PP) composite reinforced with SB showed greater stiffness compared to the raw PP material.<sup>[21]</sup> The use of SB and CaCO<sub>3</sub> as fillers in a PP matrix improved its mechanical properties and increased its thermal stability.<sup>[22]</sup> SB can also improve the mechanical and thermal properties of poly(lactic acid).<sup>[23]</sup> Furthermore, blends of collagen, natural rubber and SB can be used as a biodegradable material to promote urea release during the fertilization process, with the material degrading almost entirely after only 30 days.<sup>[24]</sup>

Gandara *et al.* produced a hydrophobic polyurethane foam matrix with SB that can absorb fats, oils and detergents from water. SB assists with oil absorption compared to a standard (or control) polyurethane matrix. The synthetic process used to make this matrix was performed in a clean and rapid manner and increasing the SB content in the polymeric matrix improved oil absorption.<sup>[25]</sup> A new material synthesized using SB and gluten showed excellent properties as a flame retardant material with low water absorption and is a potential substitute for gypsum boards as ceiling tiles.<sup>[26]</sup> Moreover, the SB based material could be used as a filler in cement materials to improve mechanical and flexural properties (in terms of rupture and elasticity) and reduce water absorption in cement blocks.<sup>[27,28]</sup> Monteiro *et al.* created an epoxy plate matrix containing 30% of SB to produce novel armor for personal protection. The armor is inexpensive to produce and showed similar properties to Kevlar®.

## REVIEW

## WILEY-VCH

Furthermore, the material gave excellent protection against bullets.<sup>[29]</sup>

## 2.2. Second-generation ethanol

Sugarcane bagasse consists of three natural polymers: cellulose (32–48 wt.%), hemicellulose (19–24 wt.%) and lignin (23–32 wt.%). Cellulose is a polycarbohydrate formed from glucose units with  $\beta$ -1,4 glycosidic bonds. Hemicellulose is also a polycarbohydrate formed from D-glucose, D-galactose, D-mannose and D-xylose units. Lignin, however, is a polyphenol compound with guaiacyl (G-unit), syringyl (S-unit) and *p*-hydroxyphenyl (H-unit) units.<sup>[30]</sup> Second-generation ethanol is obtained by fermentation of the glucose in cellulose and hemicellulose. Firstly, the polycarbohydrates are hydrolyzed using acidic or alkaline solutions, or by an enzymatic process, to release the glucose. One tonne of SB can produce 444 kg of cellulose and consequently 287 L of ethanol.<sup>[30,31]</sup> Various fermentation agents can be used to produce second-generation ethanol, with the most common being *Saccharomyces cerevisiae* (baker's yeast), as it produces a good yield of ethanol and promotes rapid conversion.<sup>[32]</sup> In addition, *n*-butanol can be obtained by an acetone-butanol-ethanol fermentation method that uses *Clostridium acetobutylicum* as the fermentation agent.<sup>[33]</sup>

## 2.3 Energy production via thermochemical conversion of lignocellulose

Thermochemical processes can be used to convert biomass into energy. The gasification process converts the lignocellulose into carbon dioxide, hydrogen, carbon monoxide and methane at temperatures above 700 °C. This process usually produces about 50% of syngas (hydrogen and carbon monoxide) as the main product. However, using specially designed catalysts (Ni/CaAlOx) can increase syngas yields up to 90%.<sup>[34–36]</sup> Syngas can then be used in the Fischer-Tropsch process to synthesize hydrocarbons.<sup>[34,35]</sup>

Lignocellulose can also be transformed into a biochar under an inert or low-oxygen concentration atmosphere, at a temperature range of 200–300 °C. This process is known as torrefaction and occurs after just one hour.<sup>[34]</sup> The biochar produced can be used as a soil improver, catalyst supporter or as an adsorbent, for dye removal or carbon dioxide capture.<sup>[36–39]</sup>

Pyrolysis of lignocellulose can be a slow or fast process and occurs in the absence of oxygen, at temperatures of 300–600 °C. The slow process transforms the lignocellulose into biochar and syngas, while the fast process produces bio-oil as the main product. The bio-oil is a mixture of phenols, aldehydes, organic acids and ketones.<sup>[34,35,40]</sup> The pyrolysis process can also be conducted via microwave irradiation, which has the advantage of being a rapid pyrolysis method, as this heating process heats the biomass core as well as its surface and requires a low temperature range (180–300 °C).<sup>[35]</sup> Furthermore, the bio-oil produced via the microwave process contains furanic compounds instead of phenolic compounds (obtained via conventional thermal heating methods) due to the non-thermal effects of microwaves.<sup>[35]</sup>

## 2.4. Cellulose derived materials from SB

Cellulose can be obtained from SB in two steps. Firstly, SB is treated with sulfuric acid solution to solubilize the hemicellulose,

followed by bleaching with sodium hydroxide to remove the lignin.<sup>[41]</sup> It is then possible to obtain nanostructured cellulose, using an acid sonication method as described by Sukyai *et al.* Thereafter, a new polymeric film was created by combining this nanocellulose with whey protein and glycerol (as a plasticizer). The film had good mechanical and barrier properties for water vapor and oxygen; which prevents the hydrolysis, degradation and oxidation of foods. It can therefore be used as a food packaging material.<sup>[42]</sup> Oliveira *et al.* also demonstrated that by bleaching SB with hydrogen peroxide in an alkaline solution, followed by an acidic hydrolysis process using sulfuric acid, the nanocellulose obtained was more crystalline.<sup>[43]</sup>

Very recently, Huang *et al.* chemically modified nanocellulose into a nano-cellulose dialdehyde via oxidative cleavage using sodium periodate in the dark for 24 h at 55 °C. The nano-cellulose dialdehyde was reacted with trimethylammonium chloride hydrazide to produce a cationic nano-cellulose which could be used as a water-based chromium(VI) adsorbent and coagulant.<sup>[44]</sup> Another SB adsorbent material (for lead(II) adsorption) was described in 2020 by Hoang *et al.* by reacting cellulose and hemicellulose with citric acid in an esterification reaction.<sup>[45]</sup>

A new gel was synthesized using microfibrillated cellulose obtained from SB, via a sonification process; with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as oxidant in aqueous sodium hypochlorite (NaClO) solution. The oxidized microfibrillated cellulose is a colorless and transparent gel, whilst microfibrillated cellulose without oxidation is white and exhibits a less consistent gel structure.<sup>[46]</sup> Aerogels blended with polyvinyl alcohol (PVA) and cellulose demonstrated interesting properties such as low density (0.016–0.122 g/cm<sup>3</sup>), higher hydrophobicity and the ability to absorb oil in water.<sup>[47]</sup> A more porous blend could be synthesized from PVA and cellulose via a sonication process. In addition, the material from this process was not cytotoxic and had a good proliferation and penetration of human skin cells; which suggests that the material could be used in tissue engineering.<sup>[48]</sup>

## 2.5. 5-Hydroxymethylfurfural (5-HMF) production using cellulose and hemicellulose

The glucose of cellulose can be easily converted into fructose in the presence of enzymes (glucose isomerase) or Lewis acids.<sup>[49]</sup> Fructose can be dehydrated to form a renewable base-chemical called 5-hydroxymethylfurfural (5-HMF), which is a valuable carbohydrate-based building block that can be transformed into other chemicals used as monomers, solvents and biofuels (Figure 2).<sup>[50]</sup>

To form 5-HMF, fructose is firstly dehydrated using strong mineral acids such as hydrochloric acid, sulfuric acid and phosphoric acid in aqueous media. This traditional process however provides yields of less than 50%, which is far from ideal from a green chemistry perspective. This could be due to 5-HMF rehydration, which forms levulinic acid, and to 5-HMF polymerizing via aldol condensations to produce humins.<sup>[50]</sup> Some researchers have therefore been investigating improving this reaction, in order to obtain higher yields of 5-HMF. To improve the reaction yield, it is possible to use heterogeneous Lewis acidic catalysts in aqueous or organic solvent-based media during the fructose dehydration process.<sup>[51]</sup> In 2011, Zhao *et al.* developed a solid cesium-based heteropolyacid catalyst (Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>) with a biphasic water and organic solvent system to achieve 74% yield, in just 1 h at 115 °C.<sup>[52]</sup> A silver

## REVIEW

WILEY-VCH

heteropolyacid catalyst ( $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ ) also gave good conversions of fructose and glucose into 5-HMF, reaching yields of up to 78% (fructose) and 76% (glucose), after 1 h at 120 °C.<sup>[53]</sup>

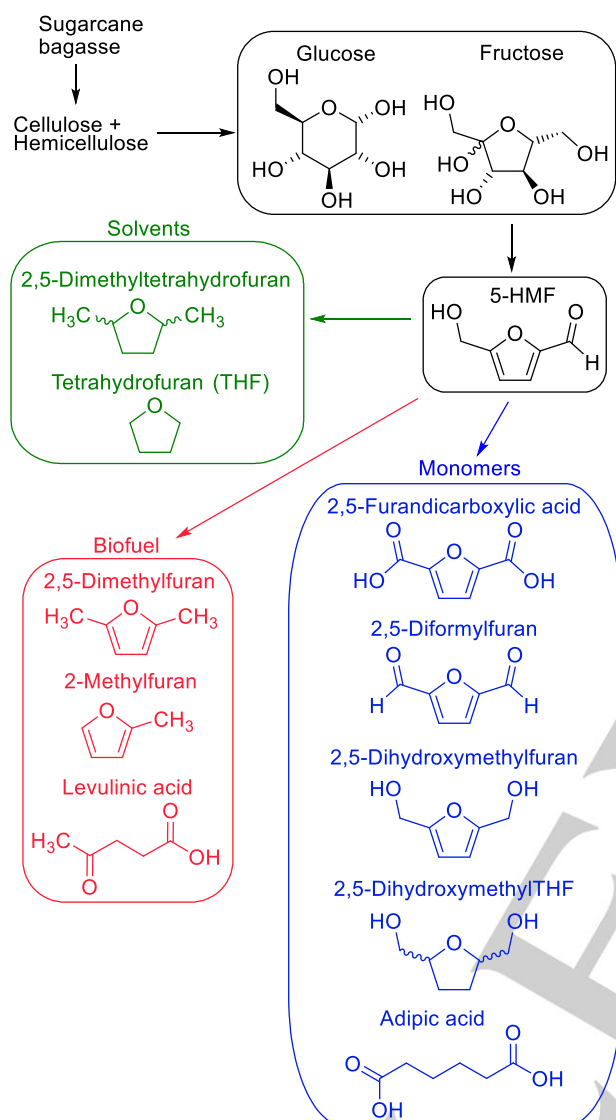


Figure 2. 5-HMF derivatives.<sup>[49]</sup>

Qi *et al.* obtained a superb fructose conversion of 94%, with the selective formation of 5-HMF in 73% yield using a sulfonated zirconium oxide catalyst. The reaction was carried out quickly (20 min) using a microwave reactor at 180 °C. This yield, however, was only achievable when using DMSO as a reaction solvent instead of water.<sup>[54]</sup> This is not ideal from a green chemistry viewpoint. Microwave hydrothermal liquefaction using cellulose and hemicellulose as starting materials was successful in just 4 mins at 149 °C. In this process, acidic seawater or brine solution was used to convert the fructose and glucose into 5-HMF. The use of seawater gave a good yield as it was found to inhibit the conversion of 5-HMF into levulinic acid.<sup>[55]</sup>

### 2.5.1 5-HMF conversion into monomers and fuels

After obtaining 5-HMF, it can be transformed into numerous chemicals, such as 2,5-diformyl furfural (DFF) which is a monomer often used for furan-based polyester production and

can be used as a substitute for petrochemical based monomers.<sup>[56]</sup> The monomer DFF can be obtained in 78% conversion via an electrochemical process using graphite and stainless steel electrodes, as the anode and cathode respectively, in the presence of oxidants such as TEMPO.<sup>[55]</sup> DFF can also be synthesized using copper(I) iodide and 1-hydroxybenzotriazole (HBT) as catalysts, achieving a conversion of 93% after 10 h in an autoclave reactor with 0.3 MPa of oxygen at 130 °C.<sup>[57]</sup>

5-HMF can be transformed into 2,5-di-hydroxymethyl-tetrahydrofuran (DHMTTHF) with high temperatures and hydrogen pressures in the presence of metallic catalysts such as Raney nickel and metal supported copper, platinum, palladium, cobalt, chromium or molybdenum species. In 2012, Alamillo *et al.* reported three new ruthenium catalysts supported on cerium oxide; magnesium-zirconium oxides and  $\gamma$ -alumina. These catalysts were used to produce DHMTTHF in high yields (88-91%).<sup>[58]</sup> DHMTTHF can be used as a solvent in the polymer industry and as a monomer for polyurethane and polyester formation.<sup>[59]</sup>

Furthermore, 5-HMF in the presence of acidic or enzymatic catalysts can react with water to produce levulinic acid (LVA), currently seen as one of the most important renewable chemicals globally.<sup>[60]</sup> LVA has been used as an alternative fuel and as a reagent to produce chemicals such as  $\gamma$ -valerolactone, succinic acid, butanone and 5-nonanone.<sup>[61-63]</sup> In addition, methyl levulinate can be reacted with fatty alcohols in a reductive etherification process, in the presence of a Pd/C catalyst to synthesise biosurfactants and biolubricants.<sup>[64]</sup>

### 2.6. Polyethylene from ethanol

Ethanol production in Brazil is large due to the internal and external market demand. In fact, sugarcane agriculture produces more ethanol than is required for fuel. Therefore, it is possible to transform the excess ethanol into other chemicals and products. Ethanol can be dehydrated to form ethylene and consequently polyethylene (PE). This process is considered green, as it uses renewable materials to produce chemicals usually derived from the petrochemical industry, and uses feedstocks that capture carbon dioxide from the atmosphere during the sugarcane growing process.<sup>[65,66]</sup>

The ethanol dehydration process occurs in the vapor phase using a fixed bed reactor of alumina or silica alumina.<sup>[67]</sup> Firstly, an ethanol and water mixture is heated to 481 °C in the reactor, then the dehydration process begins in the presence of a catalyst at a pressure of 11.3 bar. Finally, the ethylene is purified prior to polymerization, by heating at a temperature of 130-330 °C at 81-276 MPa pressure in the presence of a chromium, vanadium, zirconium, titanium or zeolitic catalyst.<sup>[68]</sup> Since 2010, Braskem have been commercially producing biobased ethylene and have branded the PE they produce as "I'm green™". The process can produce different polymers such as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE).<sup>[69]</sup> 200,000 tons of this sustainable PE are synthesized every year and it has been widely used around the world. For example, the National Aeronautics and Space Administration (NASA) have used this PE in 3D printing, enabling astronauts to use the PE to print tools and other objects.<sup>[70]</sup>



## REVIEW

## WILEY-VCH

2.7.  $\beta$ -glucan

$\beta$ -(1-3)(1-6)-D-glucan is another polycarbohydrate composed of glucose units. It is not obtained from sugarcane, but from the *Saccharomyces cerevisiae* yeast used for the fermentation. After the fermentation process, all the yeast is filtered and  $\beta$ -glucan is isolated from the yeast's cellular walls.<sup>[71]</sup>

This compound shows immunomodulatory properties and can improve the immune system of chickens<sup>[71]</sup> and pigs<sup>[72]</sup>. This suggests that using  $\beta$ -glucan as a feed supplement can reduce the use of antibiotics during animal growth. On the other hand, in dogs,  $\beta$ -glucan has been shown to modulate both the immune system and blood glucose levels, which suggests that the compound should be used carefully.<sup>[73]</sup> Furthermore,  $\beta$ -glucan can successfully control sugar levels in humans, and thus help with controlling diabetes and obesity.<sup>[74,75]</sup> Some studies also highlight the potential of this compound to be used against tumor cells.<sup>[76]</sup>

Despite these potentially interesting applications in the health and medical field, the use of  $\beta$ -glucan is limited due to its low solubility in water.  $\beta$ -Glucan is, however, totally soluble in DMSO and alkaline solutions, though this is not ideal from a green perspective. To solve this solubility problem,  $\beta$ -glucan can be reacted with acetic acid via an esterification reaction, as the addition of acetyl groups enhances solubility.<sup>[77]</sup>  $\beta$ -Glucan can also react with fatty acids in a transesterification reaction to produce a surfactant that can solubilize curcumin in water.<sup>[78]</sup> Despite these efforts, new research is needed to further modify this compound with a focus on improving its solubility.

## 3. Soybean

Although soybean (*Glycine max* L. Merril) originates from East Asia, Brazil is the second largest producer of soybean in the world, with 36 million hectares producing 115 million tonnes in 2019 (just behind USA which produced 124 million tonnes). Brazilian production has been increasing and it is predicted that Brazil will become the world's biggest producer of soybean.<sup>[79]</sup> The Mato Grosso state is the largest producer of soybean in Brazil, with a production of 32.5 million tonnes per year.<sup>[79]</sup> Brazil's internal consumption is about 44 million tonnes per year (accounting for 38% of total production).<sup>[79]</sup> The main waste produced from soybean is the soybean hull; therefore researchers have focussed on investigating soybean hull utilization. In addition, vegetable oil and proteins can be isolated from soybean and applied in the production of new materials.

## 3.1. Soybean hull

Soybean hull is an agricultural waste with a production of 9 million tonnes per year, accounting for 8% of the dry weight of the bean.<sup>[80]</sup> Although research into using soybean hull as a sustainable feedstock has been performed, the ability to use this waste as an alternative material, and the ability to transform it into new chemicals, should be improved and researched further. In 2020, Carneiro *et al.* developed a chromatographic method to obtain isoflavones from soybean hull. These are chemicals that can be used to prevent cardiovascular diseases and osteoporosis. The authors found that the green solvent ethanol could be used instead of acetonitrile; allowing the isolation of 1.2 kg of isoflavone per tonne of hull.<sup>[81]</sup> Moreover, other studies showed that polymeric beads could be produced via an

ionotropic gelatination method, using polycarbohydrates obtained from soybean hull. Isoflavones isolated from soybean were loaded into these polymeric beads and the ability of the beads to release isoflavones at different pH's was studied. A pH of 2 was the most efficient for releasing isoflavones, which is an ideal pH for release into the gastrointestinal tract.<sup>[82]</sup>

Soybean hull can also be applied in second-generation ethanol production. Schirmer-Michel *et al.* demonstrated that soybean hydrolysis can produce xylose and mannose, in 85% and 62% yields respectively. The carbohydrates were then fermented by *Candida guilliermondii* to form ethanol.<sup>[83]</sup> It is also possible to produce ethanol using xylitol extracted from hydrolyzed soybean hull, using a xylose-fermenting strain of *Spathaspora hagerdaliae*.<sup>[84]</sup> Alternatively, hydrolyzed soybean hull has been used to obtain 2,3-butanediol, using *Pantoea agglomerans* as a fermentation agent.<sup>[85]</sup>

In 2019, Cusioli *et al.* used ground soybean hull (350  $\mu$ m) without any acid or thermal treatment as a biosorbent for the removal of methylene blue (MB). The hull showed excellent results, with a maximum MB adsorption of 170 mg g<sup>-1</sup> at 25 °C and neutral pH after a contact time of 3 h. These results are compare favorably to those obtained from cucumber peel, rice husk, banana peel and orange peels, which adsorb MB at 111, 41, 21 and 19 mg g<sup>-1</sup>, respectively.<sup>[86]</sup>

Nanofibrillated cellulose (NFC) has been produced from soybean hull using an eco-friendly process with peracid as a bleaching agent, followed by an extrusion step using a 2% w/w H<sub>2</sub>SO<sub>4</sub> solution and a further deagglomeration step via sonication. The NFC produced from this process possessed a cellulose content of 92% and a crystallinity index of 73%.<sup>[87]</sup> Furthermore, it is possible to react the cellulose from soybean hull with acetic acid and chloroacetic acid to produce carboxymethyl cellulose.<sup>[88]</sup> These cellulose derivatives have potential applications as hydrogels and polymeric blends.

## 3.2. Soybean oil as a source of chemicals and materials

Soybean oil is one of the most used vegetable oils in the biofuel and polymer fields. It accounts for 20% of the total mass of soybean and contains a high quantity of unsaturated fatty acids: oleic acid (18-20%), linoleic acid (55%) and  $\alpha$ -linolenic acid (8-10%).<sup>[89]</sup> Only the most recent finds regarding the use of soybean oil will be discussed here.

In 2018 alone, 5.4 billion liters of biodiesel were produced in Brazil, of which 70% was made using soybean oil.<sup>[89]</sup> Biodiesel is often used as a petrol-diesel substitute and is a mixture of mono-alkyl esters, synthesized by a transesterification reaction between vegetable oils (triacylglycerides) and methanol or ethanol.<sup>[90]</sup> Normally, the transesterification process occurs in the presence of a strong alkaline catalyst, such as sodium or potassium hydroxide. However, these catalysts can generate soap as a by-product and thus requires a very large quantity of water to purify the final product. It is possible to use sulfuric acid as an acid catalyst or inorganic oxides such as strontium and calcium oxide as alkaline catalysts instead, which avoid saponification issues.<sup>[91]</sup> Researchers have been studying new heterogeneous catalysts to use in biodiesel production in an attempt to avoid the washing and purification steps. A new carbon-based catalyst obtained from calcinated pectin and containing calcium oxide showed high catalytic activity; producing biodiesel in 99% yield after only 4 h at 65 °C with 1 wt% loading of catalyst.<sup>[90]</sup>



## REVIEW

WILEY-VCH

Biosurfactants can be produced using soybean oil and glycerol to produce diacylglycerides. One problem with this method, however, is that glycerol is immiscible in vegetable oils. To combat this issue, a deep eutectic solvent using in conjunction with a lipase (*Aspergillus niger*) and an acrylic resin (Novozym 435) as catalyst has been used in this transesterification reaction.<sup>[92]</sup>

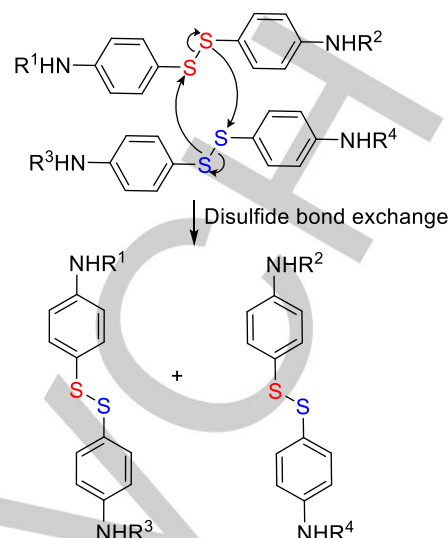
Although there is huge potential for biodiesel production using soybean oil, this renewable chemical is mostly used to synthesize new monomers and polymers. The alkenes in fatty acids can be modified and further reacted with glycerol as a crosslinker. This produces foam based polymeric materials which can then be used as dyes, anthocyanins and metal adsorbents.<sup>[93]</sup> Soybean oil can also be thermally reacted with maleic anhydride via a pericyclic "Ene" reaction.<sup>[94]</sup> Normally, this kind of reaction takes 4 h at 235 °C. Thereafter, the maleinized vegetable oil can be reacted with polyalcohols to form polyesters.<sup>[94]</sup> To reduce the reaction time, a microwave-assisted procedure can be performed, reducing the reaction time to only 15 mins.<sup>[95]</sup>

It is known that when soybean oil is exposed to daylight in the presence of oxygen, a polymeric film can be formed via an oxidation reaction. This process, however, takes a long time (1 month). In 2017, Hazer and Kalayci improved the process by adding silver nitrate as an oxidant to the reaction, producing an oxidized brownish oil in only two weeks. This oxidized soybean oil was further reacted with styrene to produce a polymeric film, which shows a fluorescence emission under UV light and has antibacterial properties.<sup>[96]</sup>

Epoxidation is considered to be the most versatile and useful process to transform soybean oil into new monomers and consequently polymers. The epoxidized soybean oil (ESO) can react with acids (e.g. sulfuric and fluoroboric acids) to open the epoxide ring and form hydroxyl groups (ESO-OH). These hydroxyl groups then react further with acetic anhydride to produce acylated soybean oil (ASO). ASO can be used as a plasticizer in polyvinylchloride (PVC) blends.<sup>[97]</sup> ESO-OH can also react with  $\epsilon$ -caprolactone in the presence of stannous octoate via ring-opening polymerization, thereby producing new polymers that can be used as biomaterials.<sup>[98]</sup> Teng *et al.* demonstrated the same ring-opening polymerization process, using ESO-OH and  $\epsilon$ -caprolactone, but also added isosorbide as a crosslinker monomer to synthesize star-shaped polymers.<sup>[99]</sup> In 2019, a new polyester was created using ESO, by reacting ESO with bis(2-hydroxyethyl) terephthalate (BHET) obtained from recycled PET, along with citric acid, mannitol and sebacic acid, to produce a polymer that could be used as a biomaterial in bone tissue engineering.<sup>[100]</sup>

The epoxide rings in ESO can also react with polycarboxylic acids at 160 °C in the presence of a catalyst.<sup>[101]</sup> Using this methodology, Wu *et al.* reacted ESO with the tricarboxylic acid: glycyrrhizic acid at various temperatures (160 °C for 1 hour, 180 °C for 2 h, and 200 °C for 2 h) and a pressure of 200 kg/cm<sup>2</sup> in a mechanical press to obtain a vitrimer with self-healing and shape memory properties. Moreover, this polymer could fully recover after cutting it into small pieces in the absence of pressure at 200 °C.<sup>[102]</sup> Another weldable and recyclable vitrimer was synthesized by Liu *et al.* in 2020 by reacting ESO with the crosslinker 4,4'-diaminodiphenyldisulfide at 180 °C. The resulting vitrimer could then be welded into a container and heated up to 180 °C at a pressure of 20 MPa in a mechanical press. Under these conditions, the disulfide bonds from two different polymeric

chains could exchange and rearrange to form new disulfide bonds between the chains, therefore the polymer was reformed (Figure 3).<sup>[103]</sup>



**Figure 3.** Disulfide bond exchange process in 4,4'-diaminodiphenyldisulfide derivatives.<sup>[102]</sup> R¹-R⁴ are EPO chains.

It is possible to react cellulose with ESO to create a new hydrophobic material. In this reaction, the OH groups in the cellulose structure attack the epoxide rings in the presence of anhydrous stannic chloride.<sup>[104]</sup> A new polymeric adhesive with flame-retardant properties was synthesized by Wang *et al.* in 2017, by reacting ESO with a dicarboxylic fatty acid with a phosphorus aromatic pendant in its structure. These new polymers have been suggested to be suitable for use as flexible electronic devices in automobiles and aircraft.<sup>[105]</sup>

Five-membered ring cyclic carbonate monomers can also be synthesized from ESO and carbon dioxide at high pressures and moderate temperatures and in the presence of a catalyst.<sup>[106]</sup> Carbonated soybean oil (CSO) was thus synthesized in 9 h with 100% conversion of epoxide by Poussard *et al.* using tetrabutylammonium bromide (TBAB) as a catalyst. The reaction occurred at 120 °C in a steel reactor pressurized to 100 bar with carbon dioxide. Thereafter, the authors performed a polymerization process using CSO and various diamines (1,2-diaminoethane, 1,4-diaminobutane and 1,5-diaminopentane) to produce non-isocyanate derived polyurethanes.<sup>[107]</sup> A polymer of CSO with chitosan could be made by reacting both components at 80 °C for 12 h to give a flexible brownish film that can be used as a moisture absorber.<sup>[108]</sup> Creating polymers using CSO with quaternary ammonium pendants produced polymers that could be used in antimicrobial wound dressings.<sup>[109]</sup> A new monomer with aminosilane pendants was synthesized by Lee and Deng in 2015, by reacting CSO with 3-aminopropyltriethoxysilane, which could be further reacted with lignin to produce renewable materials.<sup>[110]</sup> Furthermore, a terpolymerization process with CSO, carbon dioxide and propylene oxide could be produced in a one-pot synthetic route using a cobalt-zinc catalyst, with a polymerization yield of 72%.<sup>[111]</sup>

Creating photopolymerizable monomers with ESO has been widely explored in the polymeric research field, as it has been discovered that ESO can polymerize via a cationic ring-opening process in the presence of photoinitiators and UV light.<sup>[112,113]</sup> In 2017, two new monomers were synthesized in a

## REVIEW

WILEY-VCH

photoinduced click chemistry reaction catalyzed by a copper compound. The first monomer was synthesized using ESO and propargyl alcohol to form a triacylglyceride structure with pendant alkynes, and the second monomer was synthesized reacting ESO with sodium azide to form a monomer with azide pendants. Thereafter, both monomers were blended with the copper catalyst under UV light (360 nm) to produce a polymer with triazole rings (Figure 4).<sup>[114]</sup>

Acrylate and methacrylate soybean oil monomers (AcSO and McSO) can be synthesized by reacting ESO with acrylic or methacrylic acid. These monomers can be photopolymerized by a free radical polymerization process under visible or UV light (i.e. it is photoinitiator dependent). The AcSO and McSO monomers can be used in 3D printers to form biomedical scaffolds with shape memory properties, and are more competitive and renewable compared to petroleum-derived monomers.<sup>[115,116]</sup> Moreover, AcSO can be used in photopolymerized click chemistry reactions with mercapto crosslinkers to produce polymers with sulfide bonds. In addition, the crosslinker can assist with 3D printer applications<sup>[117]</sup> or

provide self-healing properties in the final polymer.<sup>[118]</sup> Li *et al.* synthesized a new monomer using ESO and monomethyl itaconate in order to avoid using acrylic or methacrylic acid, which can cause damage to the lungs, and thus produced a greener monomer.<sup>[119]</sup>

### 3.3. Soybean protein

Soybean protein (SBP) is another potential and versatile renewable compound used in chemistry and material science. It contains two major components: glycinin and  $\beta$ -conglycinin.<sup>[120]</sup> SBP can be added to improve the enzymatic hydrolysis and fermentation processes of converting sugarcane bagasse into second-generation ethanol.<sup>[121]</sup>

SBP has been widely used in controlled release materials. Liu *et al.* modified SBP with hydrazine in order to then react with carboxymethylcellulose aldehyde, thereby creating a pH-responsive material to release anti-parasite pesticides (such as

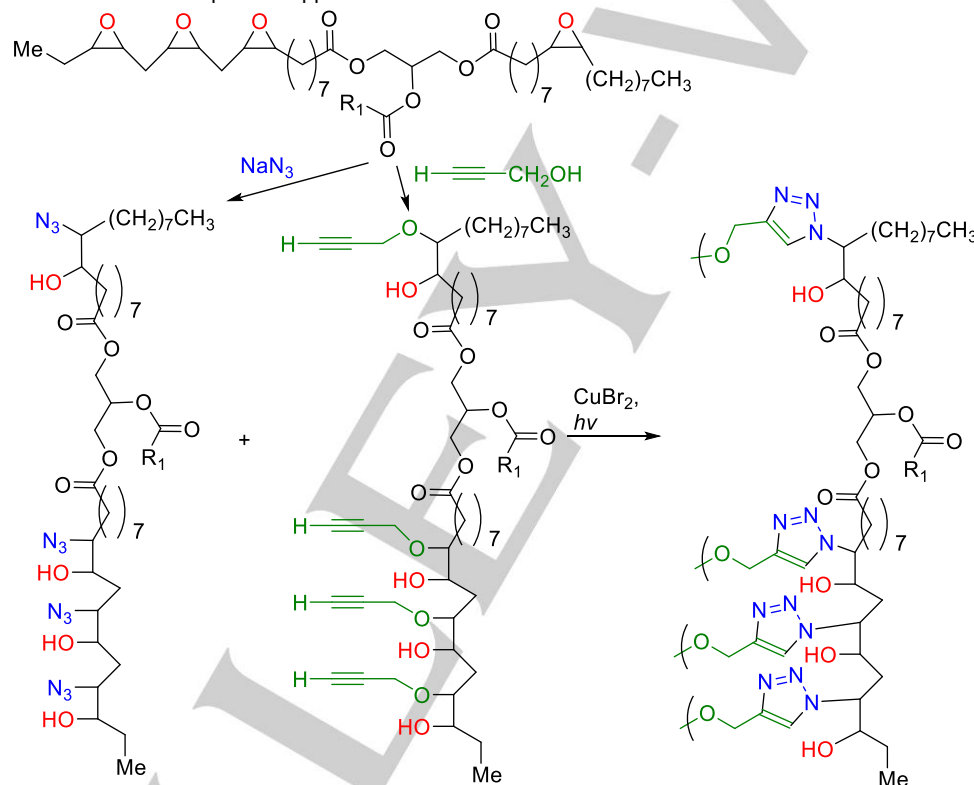


Figure 4. Soybean oil polymer with triazole units.<sup>[113]</sup>

avermectin).<sup>[122]</sup> SPB can also be modified by urea-formaldehyde block copolymers to produce a material that can release fertilizers (i.e. nitrogen, phosphorus and potassium containing species) in good yields.<sup>[123]</sup> A corn fiber-SBP hydrogel was also highlighted as a good material to incorporate and release Riboflavin (vitamin B2).<sup>[124]</sup>

Nowadays, food packaging material is a high priority to become more biodegradable and SBP has been proven to be an efficient material for this purpose.<sup>[120]</sup> Tang *et al.* created a new film using SBP and zinc oxide nanoparticles via a casting method. This film had a better oxygen barrier and higher thermal stability compared to pure SPB and also demonstrated antimicrobial activity.<sup>[125]</sup> Biomaterials can also be developed

using SBP and cellulose as demonstrated by Zhang *et al.*, who produced an edible foam with good energy absorption capacity and mechanical properties. The foam was shown not to be cytotoxic to COS-7 cells.<sup>[126]</sup> A scaffold material for bone repair and regeneration was also created by reacting SBP with cellulose nanofibrils, using TEMPO as an oxidizing agent.<sup>[127]</sup>

Finally, new technological and advanced materials can be produced using SBP, as it is a good adhesive in particleboards for construction materials and can substitute toxic and petroleum-derived adhesives.<sup>[128]</sup> Gels formed by SBP/xanthan gum with sodium chloride were shown to be promising materials for 3D printers<sup>[129]</sup> and a transparent-flexible supercapacitor can be developed using SBP and hydroxyethyl cellulose as the polymeric matrix and lithium sulfate as the electrolyte.<sup>[130]</sup>

## REVIEW

## WILEY-VCH

## 4. Starch sources

## 4.1. Cassava

Cassava from Brazil, often called *aipim*, *mandioca* or *macaxeira* (*Manihot esculenta* Crantz), is one of the most important sources of carbohydrates in Brazil and other developing countries.<sup>[131]</sup> Cassava is cropped in all of the Brazilian territories, with the Pará state producing 4 million tonnes in 2017, which was the largest single crop production in Brazil (out of a total of 20.6 million tonnes).<sup>[132]</sup> Starch (Figure 5) can be extracted from Cassava and is a mixture of two glucose containing polycarbohydrates amylose and amylopectin:

- Amylose, a linear polymeric chain connected by  $\alpha$ -(1,4) glycosidic linkages.
- Amylopectin, a branched polymer with  $\alpha$ -(1,4) glycosidic linkages and branching points made of  $\alpha$ -(1,6) glycosidic linkages.<sup>[133]</sup>

Cassava starch (CS) can be treated with acetic acid in an anaerobic digestion process to produce hydrogen and methane (biogas).<sup>[134]</sup> Biodegradable polymeric films and sustainable materials can be made using acetylated CS,<sup>[135]</sup> or raw CS combined with pea proteins, to develop edible films via a blown extrusion process.<sup>[136]</sup> Furthermore, CS composites can be made using rice husk and sugarcane bagasse to produce new renewable materials as a substitute for polystyrene, used in food packaging, protection and food trays.<sup>[137,138]</sup> Polymeric blends using CS, PVA and glycerol have been produced using a screw extruder that could be easily processed into biodegradable materials, such as films, with interesting mechanical properties.<sup>[139]</sup> Moreover, CS can be modified via a dry heating treatment to achieve polymeric hydrogels, with potential application in 3D printers.<sup>[140]</sup>

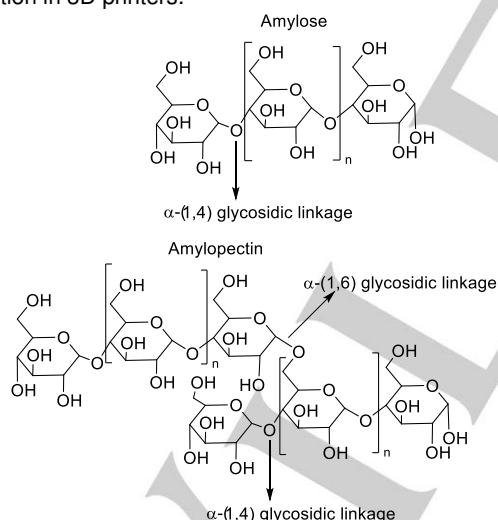


Figure 5. Amylose and Amylopectin structures as found in starch.<sup>[132]</sup>

## 4.2. Pine nut - Pinhão

Brazilian-pine (*araucaria angustifolia*) is a native tree found widely in the Paraná state, with forests containing this tree covering about 7,400 km<sup>2</sup> (8,700 tonne per year of Brazil-pine nuts).<sup>[141]</sup> The trees take about 30 years to grow to mature Brazilian-pines. As a result, human activities which devastate Brazilian-pine trees can have long-term consequences on the crop and take a long time to recover. It is therefore extremely important to demonstrate the importance and application of this crop to avoid its complete depletion from Brazil. The seeds, or

pine nuts (*Pinhão*), have a high starch content, accounting for 64% of the weight of the crop. In addition, *Pinhão* starch (PS) has a higher content of endogenous phosphorus than corn and yam starches.<sup>[142]</sup> The amylose content in PS is 19-24% and has a high amylopectin content (76-81%), which reduces the digestibility of the starch and improves its chemical stability. This in turn suggests that it can be used in nutraceutical and food formulations.<sup>[143]</sup> In two papers, Daudt *et al.* showed the potential to use PS as a pharmaceutical excipient<sup>[144]</sup> and in emulgel cosmetic formulations.<sup>[145]</sup> Acid hydrolyzed PS combined with dextrose also exhibits good coating protection for  $\beta$ -carotene, therefore increasing its chemical stability.<sup>[14]</sup>

A renewable film was developed in 2015, using hydrolyzed PS as the main product, glycerol, xanthan gum and jabuticaba peel flour as an anthocyanin source. The film has been proven to act as a good pH indicator and can be used in the food industry.<sup>[147]</sup> Furthermore, in 2020 *Pinhão* shell was incorporated into films of soybean protein and in cassava starch materials. These results indicate that the shell can be used within food packaging materials. The pine crop therefore has huge potential to become a renewable Brazilian biomass resource.<sup>[148,149]</sup>

## 5. Fruits and nuts as potential Brazilian renewable sources

## 5.1. Açai palm

The açai (*Euterpe oleracea*) fruit is a purple Brazilian fruit that grows in palm trees. It is widely cropped in the north region of Brazil and the Pará state is the biggest producer, accounting for 87% of total Brazilian production at 93,521 tonnes per year.<sup>[150]</sup> From the production of açai, two main waste materials are produced: fibrous fruit pulp and the stone (accounting for 80% of the total mass of the açai fruit).<sup>[150,151]</sup> The pulp can be treated via an alkaline process and then used as an alternative material in the particleboard industry.<sup>[150]</sup> Sulfonated carbon catalysts can be made from the açai stone via a calcination process at high temperatures (400, 500 or 600 °C) under a nitrogen atmosphere, followed by acidic (sulfuric acid) treatment and can be used as catalysts in esterification reactions.<sup>[151]</sup> Furthermore, phosphated activated carbon was produced using the açai stone in conjunction with phosphoric acid. The product possessed a high surface area (990 m<sup>2</sup> g<sup>-1</sup>) and could be used as an adsorbent for the dye basic blue 26.<sup>[152]</sup>

In addition, açai vegetable oil (ACO) can be extracted from the pulp and has a considerable oleic acid content (48%). It was illustrated in 2020 that ACO could be applied as a nanoemulsion and used as a vehicle for the antifungal medication ketoconazole. This emulsion had an encapsulation efficiency of 98% with a droplet stability of 21 days.<sup>[153]</sup> In 2019, Rosa *et al.* showed that encapsulation of desonide (a synthetic non-fluorinated corticosteroid) in ACO nanocapsules improved photostability against UV-A and UV-C light. This formulation also displayed non-phototoxic properties.<sup>[154]</sup>

## 5.2. Andiroba

*Andiroba* (*Carapa guianensis Aublet*) is a tropical tree/fruit found widely in the Brazilian amazon basin (the Amazonas state). From the *Andiroba* seed, it is possible to extract 60 wt% of vegetable oil (ADO), containing oleic, palmitic and stearic acid, which is thermally stable up to 223 °C.<sup>[155,156]</sup> ADO has been



## REVIEW

WILEY-VCH

used in common medicinal applications, such as an antiseptic and anti-inflammatory medicine and has shown cytotoxic properties against *Salmonella enterica* (a species of *Salmonella*).<sup>[157]</sup>

In 2018, researchers reacted ADO with glycerol (in a 2:1 ratio) to produce an ADO polyol derivative, using Novozym 435 as catalyst and *tert*-butanol as the reaction solvent. Thereafter, ADO polyol, glycerol SD and hexamethylene diisocyanate biuret were reacted at 60 °C for 24 h, to produce polyurethane foams with an interconnected porous network.<sup>[158]</sup>

Spherical poly(hydroxybutyrate-co-hydroxyvalerate) microcapsules, loaded with ADO, were developed in 2012 to improve their chemical stability and for ADO releasing purposes. These materials could then be applied against agricultural pests and for medicinal purposes.<sup>[159]</sup> ADO can also be loaded into chitosan films, often applied as a dressing to heal wounds, to improve the film's mechanical and thermal properties.<sup>[160]</sup>

### 5.3. Banana

Banana production is the 12<sup>th</sup> major crop in Brazilian agriculture, with two different varieties Cavendish (*Musa acuminata*) and Silver (*Musa paradisiaca*) cropped in São Paulo and the Minas Gerais states.<sup>[161]</sup> After banana consumption, the major waste is the banana peel (BP), from which phenolic compounds with medicinal properties can be extracted, or the peel can be used in its raw form in traditional medicine or as fertilizer.<sup>[162]</sup> It is possible to treat the BP with sodium hydroxide under microwave conditions to produce cellulose, hemicellulose and lignin.<sup>[163]</sup> Bankar *et al.* showed that BP extraction can assist with the synthesis of silver and gold nanoparticles at 80 °C in just 3 mins. Both these nanoparticles exhibited antibacterial activity.<sup>[164,165]</sup>

A new palladium support can be made using calcinated BP, which can act as a low-cost catalyst for arylboronic acid coupling reactions (Suzuki-Miyaura reactions), giving excellent yields for aryl bromides and iodides.<sup>[166]</sup> Carbon nanodots were synthesized using BP via a hydrothermal carbonization process at 200 °C for 24 h. This material showed high fluorescence under UV light (345 nm) with a high quantum yield (23%) and the ability to complex with iron(III) cations.<sup>[167]</sup> Furthermore, BP carbon foams formed via hydrothermal methods exhibited adsorbent properties for copper(II), lead(II), cadmium(II) and chromium(VI) cations.<sup>[168]</sup>

BP dried particles can be incorporated into chitosan films to reinforce the polymeric matrix and decrease its swelling behavior. Chitosan films with 10 wt% of BP also exhibited antibacterial activity against *Candida albicans*.<sup>[169]</sup> An edible coating can also be made using BP flour via a casting method using starch and glycerol.<sup>[170]</sup>

### 5.4. Baru nut

The Baru tree (*Dipteryx alata* Vogel) is a tropical plant that is found in south and central America and produces the Baru drupe fruit and the Baru nut. In Brazil, it is widely found in the Cerrado region and the Minas Gerais state is the major producer of this nut, with a production of 20,000 tonnes per year. It is also found in the Goiás, Mato Grosso and Mato Grosso do Sul states.<sup>[171]</sup> From this nut, it is possible to extract the baru vegetable oil (BO), which contains 47% oleic acid, and can be applied as antioxidant in health care products, due to the phenolic compounds in its composition.<sup>[172,173]</sup>

In 2012, Kogawa *et al.* reacted BO with ozone to synthesize BO ozonide derivatives with antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* (aka *E. Coli*).<sup>[174]</sup> Soaped BO was also used in polyurethane synthesis with castor oil and methylene diphenyl diisocyanate (MDI) to produce polymers that swell in water.<sup>[175]</sup> Furthermore, biodiesel from BO is a good quality fuel that passed all the standard fuel requirements when compared to fossil-fuel diesel fuel.<sup>[176]</sup> An epoxidized BO derivative with higher epoxide ring content (>99%) can be synthesized using peracetic acid in the presence of Amberlite IR120 as a catalyst. The product is a solid white grease at room temperature and can therefore be used as a lubricant and renewable epoxy monomer.<sup>[177]</sup>

### 5.5. Brazil nut

The Brazil nut tree (*Bertholletia excelsa*) is a native plant found in the amazon rainforest region (the Amazonas and Pará states) and the nut exportation is worth more than 30 million US dollars per year (27,000 tonne per year).<sup>[178]</sup> The nut shell is the principal waste of this crop, and contains a considerable quantity of selenium along with vegetable oils, with 61.5% of unsaturated fatty acids, that can also be extracted from the shell.<sup>[179]</sup> Fibers from the Brazil nut shell can be used in gelatin composites to substitute some petroleum-based elastomers.<sup>[179]</sup> The use of Brazil nut waste and vegetable oil as an alternative, green and renewable biomass has not been widely researched compared to other Brazilian crops and should be explored in future.

### 5.6. Buriti palm

Buriti is a species of palm tree (*Mauritia flexuosa*) found in the Cerrado and Amazonia rainforests, which gives a brown-orangish scale fruit. From this fruit, an orange-reddish buriti vegetable oil (BUO), with high oleic fatty acid,  $\beta$ -carotene and tocopherol (~800 mg kg<sup>-1</sup>) content can be extracted.<sup>[180]</sup> The BUO can be used in polyvinylidene fluoride composites with europium oxide to improve the red emission of the europium cations after cryo-treatment. Consequently, this material can be used as a temperature sensor.<sup>[180]</sup> BUO can also be applied in polystyrene and poly(methyl methacrylate) blends to enhance the absorption and light emission properties of these polymers.<sup>[181]</sup>

Chitosan biogels made with BUO showed potential wound healing properties and antibacterial properties against *Staphylococcus aureus* and *Klebsiella pneumonia* (which causes pneumonia). Therefore, these biogels can be applied for skin treatments.<sup>[182]</sup> BUO has also been also used in solar protective skin formulations and cosmetics.<sup>[183]</sup> Although it is often used in polymeric blends, BUO is not a primary raw material used to make polymers and materials. Despite this, the use of this renewable chemical in polymeric research is promising.

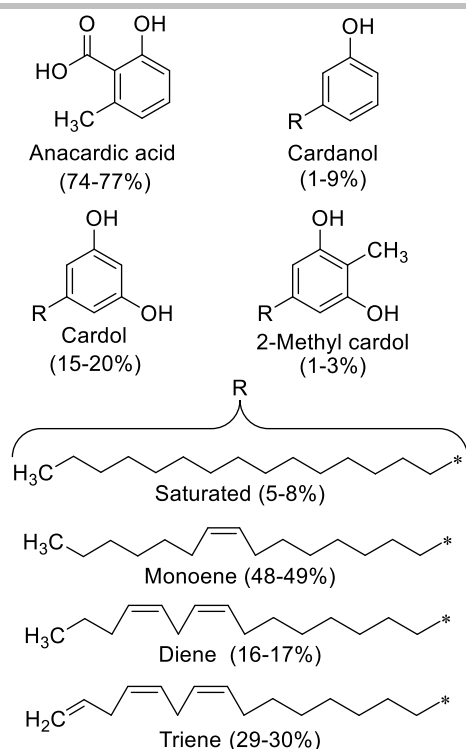
### 5.7. Cashew nut

The cashew tree (*Anacardium occidentale*) produces the cashew apple and nut, both of which are highly consumed and cropped in Brazil, with 65,300 tonnes produced in 2018. It is mainly produced in the Ceará state. From the shell, it is possible to obtain cashew nut shell liquid (CNSL), a non-edible oil with a phenolic backbone in its fatty acid structure, instead of a glycerol backbone (Figure 6).<sup>[184]</sup>



## REVIEW

WILEY-VCH

Figure 6. Chemical structures found in CNSL.<sup>[183]</sup>

CNSL can be used in polyurethane syntheses without prior modification. The phenolic part can react with isocyanate monomers to provide hydrophobic, anticorrosive and self-healing materials.<sup>[185]</sup> Various synthetic routes can be used to provide CNSL surfactants and monomers. However, CNSL is usually oxidized to give epoxide derivatives, which can be further modified to provide polyols with antioxidant properties, or reacted with acrylic acid to produce photopolymerizable monomers.<sup>[186,187]</sup>

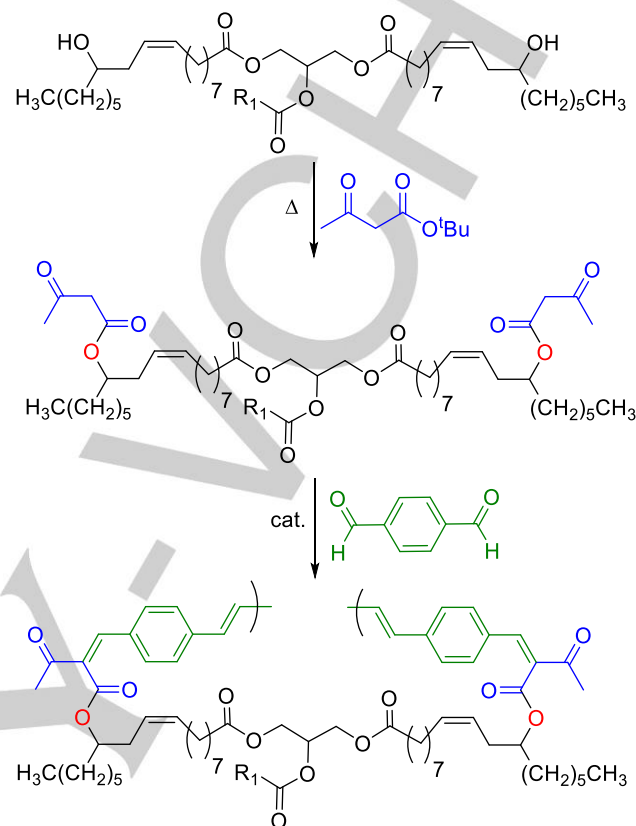
## 5.8. Castor bean

The plant *Ricinus communis* gives a non-edible fruit called castor bean, which is cropped only to obtain castor bean oil (CBO). The Bahia state is the main producer in Brazil (producing 82% of all CBO crops grown in Brazil) and the oil is used for biodiesel and polymer production.<sup>[188]</sup> CBO-based biodiesel can reduce NO<sub>x</sub> emissions and has no adverse effects on engine thermal efficiency in diesel fuel blends.<sup>[189]</sup>

CBO can easily react with isocyanates, carboxylic acids and anhydrides, due to its high ricinoleic acid (and thus OH group) content.<sup>[190,191]</sup> As a result, CBO polyurethane foams doped with titanium particles were found to be promising materials for bone repair.<sup>[190]</sup> Furthermore, polyurethane coatings showed a good ability to release nitrogen-based compounds over long time periods (about 70 days). Therefore, it is an excellent material for fertilizer use in the agricultural field.<sup>[192]</sup> In 2019, a polymer with potential biomedical applications was synthesized using epoxidized CBO and citric acid, producing a translucent final polymer with a good affinity for fibroblast cells.<sup>[193]</sup>

The transesterification reaction of CBO with *tert*-butyl acetoacetate provides a new monomer, which can be cleanly and rapidly polymerized by treatment with aromatic dialdehydes at room temperature in the presence of DABCO, via

Knoevenagel condensation reactions (Figure 7).<sup>[194]</sup> A colorless and translucent polymeric material suitable for flexible OLEDs was obtained by reacting a CBO-based polyurethane blend with bacterial cellulose. The polymer which was easy to recover and could be used as a thin film (<50 μm).<sup>[195]</sup>

Figure 7. CBO based polymer formed via a Knoevenagel condensation reaction.<sup>[193]</sup>

## 5.9. Coconut

The coconut (*Cocos nucifera*) is produced in the northeast Brazilian region (the Bahia, Sergipe and Ceará States) and Brazil is the fourth biggest producer of this crop, generating 2 billion units/year with 280 thousand hectares of crops.<sup>[196]</sup> The coconut shell is the main waste of this biomass, with some researchers using this waste to produce fibers.

Coconut fiber was used in cassava starch/lactic acid film blends, but sadly produced a film with poor tensile and impact strength properties.<sup>[197]</sup> Despite this, the use of the coconut shell improved the film's concrete strength by 15% when up to 10% was incorporated in the formulation. Furthermore, it can improve the concrete hydration process, as it creates a dense matrix and consequently increases resistance.<sup>[198]</sup>

Activated carbons produced from coconut shell have shown huge potential as adsorbents for organic textile dyes (maxilon blue GRL and yellow DY 12) and metallic ions from radioactive waste (europium(III), cerium(III), strontium(II) and cesium(I)).<sup>[199,200]</sup> Hydrogen gas can also be produced in yields of up to 57% using rhenium carbide via a shell pyrolysis process at 800 °C.<sup>[201]</sup> Thakur *et al.* created an activated carbon which displayed an ultrahigh volumetric capacitance using europium oxide in a polypyrrole matrix, and Peng *et al.* demonstrated that a new supercapacitor using activated carbon can be made from

## REVIEW

WILEY-VCH

this shell.<sup>[202,203]</sup> These studies show the promising potential for activated carbons made from coconut shell to be used as technological materials and as renewable resources.

### 5.10. Coffee

Brazil is the world leader in coffee (*Coffea arabica*) production, with 3 million tonnes produced in 2018.<sup>[204]</sup> Coffee husk is the main waste from this harvest. Therefore, the use of this material as renewable biomass is a hot area of current interest.

The coffee husk can be incorporated into polypropylene to improve its tensile strength and thermal stability and reduce the melt flow rate by 50%.<sup>[205]</sup> Cellulose, along with antioxidant and bactericide compounds can be extracted from coffee husk, which can thereafter be incorporated into thermoplastic starch films. The films showed good protection against *Listeria innocua* and *Escherichia coli*, a reduction in oxygen permeability and an enhancement in tensile strength. These materials are therefore very promising for use in food packaging.<sup>[205]</sup>

Alkaline hydrolysis can allow the isolation of bioactive compounds such as flavones, glycosides, alkaloids and terpenoids from coffee husk lignin. These compounds show anti-inflammatory, bactericide, cardiovascular protective, blood sugar regulative and anti-tumor properties.<sup>[206]</sup> Hydrochars can also be prepared by exposing the husk to a hydrothermal process at 180 °C; producing hydrochars with large specific surface areas which could therefore act as an adsorbent for methylene blue dye.<sup>[207]</sup>

Spent coffee ground (SCG) is another potential waste that can be transformed into chemicals or incorporated into materials. SCG has proven its potential application as an adsorbent of cationic (toluidine blue and crystal violet)<sup>[208]</sup> and anionic (congo red, reactive blue 5)<sup>[209]</sup> dyes in aqueous solution. Cationic dyes are adsorbed via an exothermic adsorption process whilst anionic dyes are adsorbed endothermically. Activated carbons produced from SGC have potential use as zinc(II) and mercury(II) adsorbents and in carbon paste electrodes for lead(II) and cadmium(II) quantification.<sup>[210,211]</sup>

Using microwaves, it is possible to extract polysaccharides (galactomannans and arabinogalactans) from SGC in 5 mins at 200 °C.<sup>[212]</sup> These polysaccharides are widely used in the food industry and by performing an alkaline hydrogen peroxide treatment, it is possible to obtain a renewable biopolymeric film.<sup>[213]</sup> In addition, vegetable oil can be removed from SGC using *n*-hexane, and can then be transformed into polyhydroxyalkonates by the bacteria *Ralstonia eutropha*, as a potential bio-based substitute for petrol-based polymers.<sup>[214]</sup> Finally, it was possible to recover high yields (92%) of phenolic compounds, such as chlorogenic acid from SGC, using 1,6-hexanediol and choline (in a 7:1 ratio) in a deep eutectic solvent-based process.<sup>[215]</sup>

### 5.11. Grape

Although the grape (*Vitis labrusca*, *Vitis ourquina* and *Vitis vinifera*) is not a native Brazilian fruit, its production has been increasing in the Rio Grande do Sul state due to the wine industry (1.6 million tonne per year).<sup>[216]</sup> The grape seed is the major waste and provides grape seed vegetable oil (GSO). GSO contains a relatively high quantity of  $\alpha$ -tocopherol (57 mg kg<sup>-1</sup>), which can be removed via a pressurized liquid extraction using *n*-hexane.<sup>[217]</sup> GSO can also be modified with peracid to produce epoxide derivatives that can be further transformed into

polyalcohols which can then be reacted with isocyanates to give renewable polyurethanes.<sup>[218]</sup> Amine derivatives can also be synthesized using GSO and cysteamine hydrochloride under UV light irradiation, via a thiol-ene reaction between the double bond of GSO and the thiol group of cysteamine (Figure 8).<sup>[218]</sup>

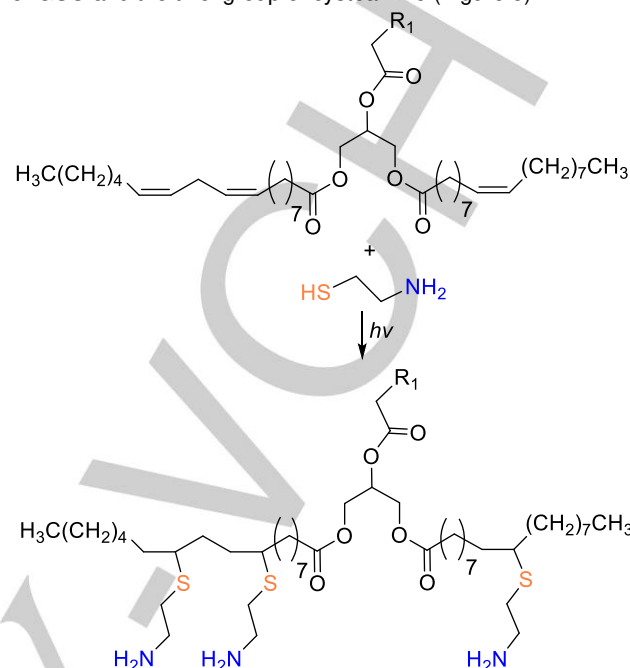


Figure 8. Reaction between GSO and cysteamine under UV light.<sup>[217]</sup>

### 5.12. Jaboticaba

The jaboticaba fruit (known as *Myrciaria jaboticaba* or *Myrciaria cauliflora*) has a dark-purple peel and a sweet white pulp and can be found widely across the whole of Brazil. Normally, it is used to produce licorice and jam, and about 50% of this fruit (the seed and peel) is treated as a waste material. From the seed, it is possible to extract vegetable oils with 62% of unsaturated fatty acids.<sup>[219]</sup>

The peel has a greater quantity of anthocyanins and ellagitannins compared to the seed. It is also possible to recover other high value compounds, such as citric acid, malic acid and  $\alpha$ -tocopherol from the peel. These compounds have shown promise against bacteria such as *Escherichia coli*, *Streptococcus aureus* and *Listeria monocytogenes*. Furthermore, these compounds have a potential application against tumor cells.<sup>[220]</sup>

### 5.13. Macaw palm

The macaw palm (*Acrocomia aculeata*) or *macaúba* gives a fruit similar to coconut that can be found in the cerrado region. Nowadays, the macaw palm is widely cropped in Brazil to substitute soybean oil in biodiesel production. This fruit contains a high quantity of macaw vegetable oil (MO), which produces 4,000 L of oil per hectare of crop. This is much higher than the soybean which produces only 500 L per hectare and around 79.5% of the MO oil contains unsaturated fatty acids.<sup>[177,221]</sup> The MO transesterification reaction to produce biodiesel can be performed with methanol or ethanol, using aluminum oxide, niobium oxide or activated carbon fiber as catalysts.<sup>[222]</sup>

MO like other vegetable oils can be reacted with peracid to synthesize epoxidized compounds.<sup>[177]</sup> Quirino *et al.* synthesized

## REVIEW

WILEY-VCH

a polyol derivative by reacting epoxidized MO with formic acid and water. Thereafter, the polyol was reacted with methylene diphenyl diisocyanate to obtain polyurethanes, before then incorporating coconut fibers into the polymer structure to increase its mechanical properties.<sup>[223]</sup> Epoxidized methyl-esters from MO can also react with polyhydroxyalkanoate to give translucent films with increased water solubility, water permeability and tensile strength.<sup>[224]</sup>

#### 5.14. Orange

Brazil is the world's largest producer of oranges, with 18 million tonnes produced per year (28.8% of world production), 70% of which comes from only one species (*Citrus sinensis* L. Osbeck).<sup>[225]</sup> The fruit is used to produce juice, jam and sweets and the orange peel is the main industrial waste from this fruit.

Limonene (orange essential oil) is a cycle terpene formed by two isoprene units, which can be extracted from the peel and used as a flavor agent in the food industry. In addition, it is an excellent renewable chemical used in the polymer research field. Limonene has two alkenes in its structure that can react (via a vulcanization process) with sulfur at 185 °C, or with mercapto groups under UV light, to synthesize polymers.<sup>[226,227]</sup> The alkenes can also be converted into epoxides and thereafter reacted with anhydrides to form polyesters. Furthermore, limonene oxide can also react with carbon dioxide to obtain five-membered cyclic carbonates, which are widely used in polyurethane production.<sup>[227]</sup> The polymerization reactions that can be performed with limonene are summarized in Figure 9.

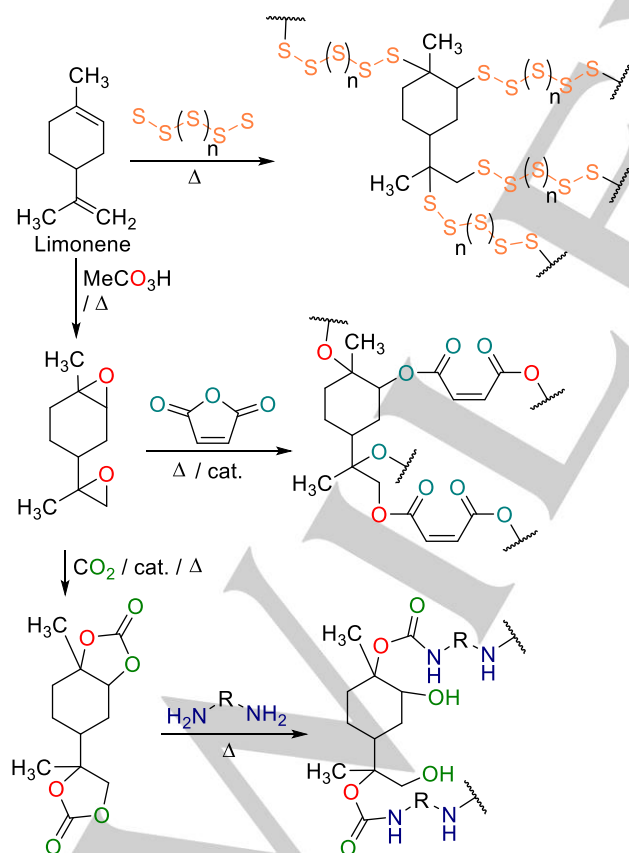


Figure 9. Polymerization reactions using limonene as a monomer.<sup>[225,226]</sup>

In addition, histidine (flavanone glycosides with anti-inflammatory and anti-tumor properties) can be recovered in

89% yield from the interior of the peel, by solvent extraction using methanol followed by crystallization in water/dichloromethane. The histidine can be converted into diosmetin (a glycoside free flavanone) by hydrolysis with sulfuric acid at 99 °C in 88% yield.<sup>[228]</sup>

The anionic polycarbohydrate formed by  $\alpha$ -1-4-linked *D*-galacturonic acid (aka pectin) can be removed from orange peel using acidic or alkaline solutions.<sup>[229]</sup> This pectin can be used in renewable gels that work as solution traps. It is widely used in the food and pharmaceutical industry as a thickener agent and can make biofilms used in coating packaging.<sup>[229,230]</sup> Orange peel can be fermented by the bacteria *Lactobacillus delbrueckii* and *Lactobacillus bulgaricus* to provide lactic acid, in yields of 86% and 95%, respectively. Lactic acid is widely used in polymer research to obtain biomaterials.<sup>[231]</sup> Cellulose can also be removed from orange peel by microwave hydrothermal treatment. Thereafter, bactericide material can be produced by incorporating silver nanoparticles into the structure, showing strong activity against Gram-positive and Gram-negative bacteria.<sup>[232]</sup>

#### 5.15. Papaya

Papaya (*Carica papaya* Linn.) is a tropical fruit that originates from central America and has been cropped in Brazil since 1578. Brazil produced about 1 million tonnes of Papaya per year and about 30% of this fruit (the peel and seeds) is waste material.<sup>[233,234]</sup>

Papaya vegetable oil (PO), with a high oleic acid content (71%), can be extracted from the seed, with 78% in total of the waste consisting of unsaturated fatty acids.<sup>[234]</sup> PO can be reacted with methanol to produce biodiesel with low carbon dioxide and carbon-based emissions when blended with standard diesel.<sup>[235]</sup> The seed shell can be calcinated to form an activated carbon that can adsorb organic dyes or metal ions (lead(II) and cadmium(II)) in aqueous media.<sup>[234]</sup>

It is possible to extract retinol,  $\alpha$ -tocopherol, ascorbic acid and papain (Enzyme Commission Number: EC 3.4.22.2), an enzyme widely used in medicine to treat intestinal disorders and skin wounds.<sup>[236]</sup> Papain can be incorporated into chitosan films and combined with zinc oxide to obtain biomaterials with low cytotoxicity to skin.<sup>[237]</sup> The papaya peel can be pyrolyzed and further modified with EDTA to produce luminescent carbon nanodots with the ability to undergo chromium complexation.<sup>[237]</sup>

#### 5.16. Passion fruit

Passion fruit (*Passiflora edulis* Sims) is a native Brazilian tropical fruit known as *maracujá*. Brazil is the largest global producer of passion fruit, with 602 thousand tonnes produced in 2018 (accounting for 57% of world production). Normally, the fruit is used in jams and in juices, with 52% of the fruit discarded as the peel and seeds.<sup>[234,239]</sup>

Usually, the peel is used to obtain pectin, which can be extracted in good yield using acidic solutions.<sup>[240]</sup> Passion fruit peel can also be used in anaerobic digestion processes to produce methane (biogas).<sup>[239]</sup> Moreover, the vegetable oil (PSO) can be extracted from the passion fruit seeds, and has a composition of 86% unsaturated fatty acids. When PSO is extracted using hexane, other compounds such as carotenoids, salicylic acid, campesterol,  $\beta$ -sitosterol and stigmastanol can be recovered as well. These compounds have bactericidal activity against Gram-positive and Gram-negative bacteria.<sup>[236]</sup> Finally,



## REVIEW

## WILEY-VCH

epoxidized PSO can be used as a bio-lubricant and in the syntheses of polyurethanes.<sup>[242,243]</sup>

### 5.17. Pineapple

Pineapple or abacaxi (*Ananas comusus*) is another native Brazilian fruit with a production of 1,7 million fruit units in 2018 and it is broadly used in the juice industry.<sup>[244]</sup> This industry treats pineapple pulp and its peel and crown as waste material. From the pulp, an enzyme called bromelain (Enzyme Commission Number: EC 3.4.22.33) can be extracted, which: can be used to reduce cardiovascular diseases; possesses anti-inflammatory activity; can repair and protect skin wounds; can inhibit cancer cells; and can act as a meat tenderizer.<sup>[244]</sup> From pineapple stem, another bromelain enzyme (Enzyme Commission Number: EC 3.4.22.32) can be extracted, which also shows health benefits in humans.<sup>[245]</sup>

The peel can be modified with succinic acid to obtain a complexing agent for copper(II), cadmium(II) and lead(II).<sup>[246]</sup> A renewable hydrogel was obtained by dissolving pineapple peel in 1-butyl-3-methylimidazolium chloride at 100 °C for 5 h. At the end of the process the hydrogel obtained can be used as a dye adsorbent.<sup>[247]</sup> From the pineapple peel, polyhydroalkanoates or polyhydroxybutyrates can be obtained using *Ralstonia eutropha* or *Bacillus drentensis* bacteria, respectively.<sup>[248,249]</sup>

## 6. Summary and Outlook

Brazil has a huge quantity of crops and native plants that can be used as renewable sources. The currently wasted and renewable materials sourceable from Brazilian crops are not limited to these presented in this review and new research should be done to valorize their use and application in chemistry and material research. The São Paulo State Research Foundation (FAPESP) has a program called BIOTA that

supports the study and use of Brazilian native plants and biomass (especially from cerrado region) and this is gradually being updated with new research every year.<sup>[250]</sup> Brazil has been improving the preservation and use of these crops, as well as increasing waste utilization. However, some plants such as soybean and sugarcane have been explored much more than other Brazilian native plants. For instance, only a handful of research papers have described the potential application of jaboticaba, buriti and Brazil nut vegetable oil. These biomasses should be further studied in the materials research field. Furthermore, coconut has a huge potential to be used in other research areas, not just to make composites from its raw form. Therefore, it is extremely important to develop new studies and new materials from these plants. Table 1 summarizes the most common compounds that can be utilized from each crop.

Research is currently finding and creating sustainable and renewable methods to substitute petroleum-based materials and chemicals. However, in order to fully develop the potential applications of these waste materials, studies must not only focus on using these biomasses as a cheap alternative fuel, but to also obtain higher value compounds from these renewable sources, whilst simultaneously avoiding further crop depletion across Brazil. Thus, this review was created to help inform researchers in their studies about the current state of utilizing Brazilian biomass, to encourage researches to be bold and ambitious when extracting compounds from renewable sources, and to expand the viability of Brazilian native plants as a green resource.

**Table 1.** Most common renewable chemicals obtained from each Brazilian biomass, their annual production and crop residue.

	Enzymes	Fatty acids	Flavonoids	Fine chemicals and vitamins	Polycarbohydrates /polymers	Terpenes	Annual Production / tonnes	Crop residue / tonnes <sup>a</sup>
<b>Açaí</b> <sup>[150]</sup>		X	X	X	X		93,521	74,816
<b>Andiroba</b>		X		X	X	X	<sup>b</sup>	<sup>b</sup>
<b>Banana</b> <sup>[161,162]</sup>				X	X		6,962,134	2,436,747
<b>Baru</b> <sup>[171]</sup>		X		X	X		20,000	19,000
<b>Brazil-nut</b> <sup>[178,251]</sup>		X		X	X		69,900	61,512
<b>Brazil-pine</b> <sup>[141]</sup>				X	X		8,700	2,262
<b>Buriti</b>		X		X	X		<sup>b</sup>	<sup>b</sup>
<b>Cassava</b> <sup>[132,252]</sup>				X	X		20,600,000	18,540,000
<b>Cashew nut</b> <sup>[184]</sup>		X		X	X		65,300	6,210
<b>Castor bean</b> <sup>[188,253]</sup>	X	X		X	X		93,025	51,163
<b>Coconut</b> <sup>[196,254]</sup>		X		X	X		2,000,000,000 <sup>c</sup>	907,530
<b>Coffee</b> <sup>[204]</sup>		X	X	X	X	X	3,000,000	1,350,000
<b>Grape</b> <sup>[216]</sup>		X		X	X		1,600,000	640,000
<b>Jaboticaba</b> <sup>[255]</sup>		X	X	X	X		2,577 <sup>d</sup>	1,288.5 <sup>d</sup>
<b>Macaw</b> <sup>[221,256,257]</sup>		X		X	X		100,000	50,000
<b>Orange</b> <sup>[225,258]</sup>				X	X	X	18,000,000	9,000,000
<b>Papaya</b> <sup>[233,234]</sup>	X	X		X	X		1,000,000	300,000
<b>Passion Fruit</b> <sup>[234,239]</sup>		X	X	X	X		602,000	343,140
<b>Pineapple</b> <sup>[244]</sup>	X			X	X		1,700,000 <sup>c</sup>	1,258,000
<b>Soybean</b> <sup>[79,80]</sup>		X	X	X	X		115,000,000	9,200,000
<b>Sugarcane</b> <sup>[10]</sup>				X	X		620,000,000	173,600,000

<sup>a</sup> Estimated value considering hull, bagasse, seeds, fruits peel and so on.

<sup>b</sup> Value not found (family-based agriculture).

<sup>c</sup> Quantity of units per year.

<sup>d</sup> Production in São Paulo state only.



## REVIEW

WILEY-VCH

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**Entry for the Table of Contents**

Renewable and sustainable chemicals and materials can be obtained from natural resources. Consequently, increasing our knowledge about native plants is essential for new avenues of research in this area. This article focusses on Brazil, which offers a diverse range of biomass, all of which can be used to produce sustainable and renewable materials.