Biomass Residues in Brazil: Availability and Potential Uses

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Abstract Agroindustrial and forestry residues, which are by-products of key industrial and economical activities, stand out as potential raw materials for the production of renewable fuels, chemicals and energy. The use of wastes is advantageous as their availability is not hindered by a requirement for arable land for the production of food and feed. In addition, waste utilization prevents its accumulation, which is of great environmental concern due to its potential for contamination of rivers and underground water. In Brazil, the agroindustry of corn (13767400 ha), sugarcane (7080920 ha), rice (2890930 ha), cassava (1894460 ha), wheat (1853220 ha), citrus (930591 ha), coconut (283205 ha), and grass (140000 ha) collectively occupies an area of 28840726 ha (FAOSTAT, [http://www.](http://www.faostat.fao.org/site/567/default.aspx#ancor) [faostat.fao.org/site/567/default.aspx#ancor](http://www.faostat.fao.org/site/567/default.aspx#ancor)) and generates

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597 million tons of residue per year. By itself, this scale of operation calls for new solutions aiming for the appropriate utilization of these valuable resources. However, innovative dealings must be environmentally and economically acceptable and, most importantly, have social meaning. Indeed, great social benefits could draw from novel yearround activities as alternatives for the typical seasonal jobs in agroindustry. Considering the production of biomass ethanol, the abundance of feedstock near the site of processing must be taken into account, as low-density biomass involves significant handling and transportation costs. Within this context, the crushed stalk of sugar cane (bagasse) and straw are obvious choices, although bagasse is often burned for the production of steam (heat) and power/electricity in sugar-ethanol mills and important amounts of straw are needed to keep the soil nutrients balance. Other agricultural by-products of importance in Brazil, such as corn straw, wheat straw, rice straw and rice hulls, grass and forestry materials and residues from citrus, coconut and cassava processing, also deserve attention as local feedstock for the development of new and profitable activities. As each type of feedstock demands the development of tailor-made technology, the diversity of the aforementioned raw materials could allow for new solutions for the production of chemicals, fuels and energy in accordance with the local availability of these materials.

Keywords Brazilian agroindustrial residues \cdot Agroenergy \cdot Biomass ethanol \cdot Renewable resources \cdot Sugar cane bagasse · Sugar cane straw

Foreword

The global demand for liquid biofuels more than tripled between 2000 and 2007, indisputably showing the increasing

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trend towards the use of fuels derived from plant feed stock [\[1–2](#page-9-0)]. Apparent in Brazil due to its current fleet of 80 million flex-fuel cars [[3\]](#page-9-0), this prospect is reinforced by the EU-wide target of 5.75% biofuels for transportation in 2010 and 10% in 2020 [[4\]](#page-9-0), and the US proposal to replace 30% of gasoline by 2030 [[5\]](#page-9-0). Moreover, ethanol presently replaces approximately 40% of gasoline in Brazil and 3% of gasoline in the world [[6,](#page-9-0) [7\]](#page-9-0). The growing demand for liquid fuels is leading to the development of second-generation technologies because of significant issues related to: (i) oil prices, energy supply security and reduction of oil imports; (ii) environment concerns, support for agricultural activities and greenhouse gas mitigation; and (iii) social and geographic issues [\[2](#page-9-0)]. Within this context, the importance of developing and improving technologies for the production of renewable fuels, such as ethanol, methanol, butanol and diesel as well as the equally important biogas used for heating and cooking, is crucial. Renewable feed stocks presenting different substrates, such as sugars, starch, lignocellulose and vegetable oils, can be processed via chemical, thermochemical or biochemical routes to obtain the target product.

Plant cell walls are the source of lignocellulose, a complex and chemically rich material also known as biomass, whose structure is chiefly represented by the physico-chemical interaction of cellulose, a linear glucose polymer, with hemicellulose, a highly branched sugar heteropolymer, with lignin, a very high molecular weight and cross-linked aromatic macromolecule. Liquid fuel production from lignocellulose can be done via a thermochemical route using pyrolysis or gasification to produce synthesis gas $(CO + H_2)$, from which a wide range of long carbon chain fuels, such as synthetic diesel and jet fuel, can be produced. The conversion of lignocellulose to ethanol can be done biochemically after biomass hydrolysis via either the ''acid-based'' or the ''enzyme-based'' route. The enzyme-based route which is a highly complex multienzymatic process requires biomass pretreatment because the lignocellulosic materials are structured for strength and resistance to biological, physical and chemical attack. The biochemical route is advantageous due to its higher conversion efficiency, minimization of substrate degradation (often observed in the acid-based route) and the use of more moderate and non-corrosive physical–chemical operating conditions. Irrespective of the process for the hydrolysis of the biomass polysaccharides, the residual polyaromatic hydrophobic lignin, which has the potential to release 27000 kJ per kg, is of foremost importance as solid fuel or as raw material for the chemical industry [\[8](#page-9-0)]. This work presents and briefly discusses the availability and potential uses of representative biomass wastes in Brazil derived from cultures of maize, sugarcane, cassava, wheat, citrus, coconut, rice, gramineous and forestry activities.

Sugarcane

In Brazil, currently 325 sugar-ethanol plants process approximately 649 million tons of sugarcane per year, and approximately equal amounts of its sucrose-rich juice are used for sugar and ethanol production. This industry has been growing steadily as ethanol productivity has been increasing approximately 4% per year in the last 29 years. Moreover, it is estimated that 86 new distilleries will be operating by 2015 [\[6](#page-9-0), [9\]](#page-9-0). The energy balance of 8.9 (renewable energy generated/fossil energy consumed) of sugarcane ethanol production compares favorably to that of corn ethanol (1.3), and shows that Brazil is a frontrunner in ethanol production whose production cost is estimated in US\$ 35/barrel [[6,](#page-9-0) [7\]](#page-9-0).

First-generation ethanol, from sugarcane in Brazil and corn in the US, is mature and has well-established commercial technologies and markets. Nevertheless, starch ethanol is more complex and costly than that from sugarcane because its production includes additional steps for starch gelatinization through heating and starch enzymatic hydrolysis before glucose fermentation to ethanol. In both cases, significant biomass residue, either corn straw or sugarcane bagasse and straw, are generated and considered as potential raw materials for biomass ethanol production.

According to data presented in Table 1, in 2008, Brazil produced 415 million tons of sugar cane residues, 194 million tons of sugar cane bagasse and 220 million tons of sugar cane straw $[10]$ $[10]$. The energy content of these wastes supports its use for bioethanol production, as onethird of the sugarcane plant total energy is present in bagasse and one-third is present in straw (tops and leaves). It is estimated that 88% of bagasse (19400 kJ/kg) has been used for energy cogeneration in the sugar-ethanol production plants. An increase in bagasse surplus is forecasted due to the optimization of the boiler efficiency and the electricity generation system $[6, 7, 11]$ $[6, 7, 11]$ $[6, 7, 11]$ $[6, 7, 11]$ $[6, 7, 11]$ $[6, 7, 11]$ $[6, 7, 11]$. From the total Brazilian annual production of 220 million tons of sugar cane straw, about 50% is left in the field to avoid erosion, for the maintenance of soil agronomic properties related to its carbon–nitrogen ratio, K, P, Ca, Mg and S content, and for the preservation of soil microbiota. Straw has also been

Table 1 Estimated production of sugarcane and its residues (wet biomass) in Brazil in 2008 [[10](#page-9-0)]

Raw material	Production (1000 ton)	Residues	Amount of residues $(\%)$	Production of residues (1000 ton)
Sugarcane 648973		Bagasse	30	194692
		Straw and leaves	34	220651
Total				415343

studied for electricity generation and the production of metallurgical coke as well as of silicon carbide with applications as semiconductors, in abrasives, refractories, armor aircraft and microelectronics due to its high silica content [\[12](#page-9-0)]. Moreover, as the traditional practice of burning the sugarcane leaves prior to manual harvesting is being phased out (according to Brazilian Federal Law 2661 and State of São Paulo Law N° 11241 dated 19/09/2002 [\[13](#page-9-0)]), the mechanized harvest gradually will take its place and higher quantities of strategically placed sugarcane straw will be available for either co-generation or as ethanol feedstock.

Although the urgent increase in ethanol production in the near future will largely rely on the expansion of the sugarcane plantations for the production of first-generation ethanol and on the parallel increase of the number of distilleries, it is expected that the production of ethanol from sugarcane biomass (bagasse and straw) will eventually be significant. The sugarcane biomass is advantageous due to its industrial surplus amounts and most importantly, because they are strategically located near the sugar-and ethanol-producing units. The deployment of this technology in Brazil is also favored because the biomass ethanol production process can be annexed to the sugar/ethanol units already in place, requiring lower investments, infrastructure, logistics and energy supply.

As 12% of bagasse and 50% of straw (leaves) would be available for second generation ethanol, the amount of fuel produced, considering the biomass average cellulose content of 30%, would be significant. Indeed, as one ton of sugar cane contains 340 kg of leaves (10% humidity) and 300 kg of bagasse (50% humidity) it would be possible to produce, considering the theoretical yields of the biochemical route, a surplus 36.5 l of ethanol on top of the 80 l already produced from the sugarcane juice (sucrose) extracted from one ton of cane.

Corn

Maize is the most widely grown crop in the Americas. While the United States produces almost half of the world's harvest (42.5%, corresponding to over 220 million tons), other top producing countries include China (151 million tons) followed by Brazil (52 million tons), Mexico, Argentina, India and France. Worldwide production was around 800 million tons in 2007, just slightly higher than rice (650 million tons) or wheat (600 million tons) $[1]$ $[1]$.

In the US, ethanol is produced from corn starch $[14-21]$, and ethanol production from corn stover has been the subject of an intensive research effort in the US, due to its potential to generate industrial amounts of ethanol [\[22](#page-9-0)].

The amount of crop residue (maize straw, stem, leaves and cobs) generated after corn harvest corresponds roughly to the same amount of the harvested corn. As such, considering that the US corn biomass availability is in the range of 30–60%, as is that of sugarcane straw part of the residue is supposed to be left in the field, around 66–132 million tons of corn residue could be used in biochemical conversion processes with a potential of supplying 11–22 billion liters of ethanol fuel from cellulose [\[23–25](#page-9-0)].

In Brazil, corn is mainly used as food or feed, and this culture produces residues amounting to 46 million tons of straw, stems and leaves. Even considering that 50% of the total amount of lignocellulosic residues should be left in the field, over 4.4 billion liters of cellulosic ethanol could be produced from the surplus biomass. Technology development would be a win–win process with Brazilian collaboration with leading international institutions in this area. The use of corn flour-processing residue, maize germ and wraps, which correspond to 20% by weight of maize grains, would also be a valid option for biotechnological conversion processes. Table 2 presents the estimated production of corn residue in 2008.

In China, large amounts of concentrated agricultural waste corncob are produced annually, leading to environmental pollution due to the lack of effective utilization. Enzymatic hydrolysis of corncob and corn stover followed by ethanol fermentation using the cellulosic hydrolysate has been reported [\[26](#page-9-0)[–29\]](#page-10-0).

Cassava

Cassava, also called yucca, or manioc, is a woody shrub native to South America, which is extensively cultivated as an annual crop in tropical and subtropical regions for its edible starchy tuberous root and used to produce tapioca flour, a major source of carbohydrates.

World production of the cassava root was estimated to be 214 million tons in 2007. Nigeria, which produced

Table 2 Estimated production of residues (wet biomass) from maize in Brazil in 2008 [\[10\]](#page-9-0)

Raw material	Production Residues (1000 ton)		Amount of residues $(\%)$	Production of residues (1000 ton)
Maize (grains)	59012	Germ and wraps	20	11802
		Straw, stems and leaves	-78	46029
		Corn cob	22.	12983
Total				70814

34 million tons in 2007, is the world's largest producer. According to statistics from FAO, the Food and Agriculture Organization of the United Nations, Thailand, with 27 million tons produced in 2007, is the largest exporting country of dried cassava, with a total of 77% of the world export in 2005. The Brazilian cassava production of 26.5 million tons in 2007 is similar to that of Thailand.

Cassava is an important alternative source of starch for the production of glucose syrups that can be used for ethanol production from either the whole cassava tuber or the starch extracted from it [\[21](#page-9-0)]. Starch extraction can be carried out through a high-yield large-volume industrialized process that can be considered as the equivalent of the wet-milling process for ethanol production from corn. The hydrolysis of cassava flour has been proposed for the production of glucose considering that cassava flour production is more simple and economical than cassava starch production [\[30](#page-10-0)]. Ethanol fuel production from whole cassava is equivalent to ethanol production from corn by the dry-milling technology; nevertheless cassava should be transported as soon as possible from the cropping areas due to its rapid deterioration. One of the solutions to this problem is the use of sun-dried cassava chips [\[31](#page-10-0)]. The farmers send the cassava roots to small chipping factories where they are peeled and chopped into small pieces, which are sun-dried for 2–3 days. The first step of the process in the distillery is the grinding of the dried cassava chips or fresh roots. Milled cassava is mixed with water and then undergoes cooking followed by the liquefaction process. The liquefied slurry is saccharified to obtain the glucose, which will be assimilated by the yeast during the next fermentation step. If fresh roots are employed, a fibrous material is obtained in the stillage after distillation. This material can be used as animal feed similarly to the DDGS produced in the corn-based process. The wastewater can be treated by anaerobic digestion to produce biogas, which can be used to produce steam and power for the process [[32\]](#page-10-0).

The residues of the cassava crop, the shoots of the plant after the removal of the tuberous cassava roots, are estimated to weigh 144–257% of the root weight (Table 3). The use of the cassava stems and leaves as forage or addition of the waste roots to prepare feed flour is justified by its nutritional value and high forage yield per hectare [\[23](#page-9-0)]. Several steps are involved in the processing of cassava roots to obtain the industrial products starch and cassava flour (tapioca): peeling and washing, grating, pressing, disintegration, sifting, drying, milling and screening. The residues which are generated, such as bran from the root peeling, cassava waste liquor from pressing and waste fibers form sifting can be used in combination with aerial parts of the plant to prepare fodder due to its

Table 3 Estimated production of residues (wet biomass) from cas-sava in Brazil in 2008 [\[10\]](#page-9-0)

Raw material	Production (1000 ton)	Residues	Amount of residues $(\%)$	Production of residues (1000 ton)
Cassava	26337	Bran	16	4214
		Straw, stems and leaves	200	5.673
Total				56887

balancing content of starch, protein and other nutrients necessary for animal growth.

Cassava dry pulp, a residue of starch production, contains around 50% starch and 43% insoluble dietary fiber on a dry weight basis [\[33](#page-10-0)]. As pulp disposal causes deleterious effects to the environment, there are reports of recovering its starch via sonication or by enzymatic hydrolysis of its fiber content using a multi-enzyme mixture of cellulase and pectinase [[34\]](#page-10-0). This material, also called residual cassava fibrous waste or bagasse, contains 30–50% starch on a dry weight basis plus cellulose and hemi-cellulose at levels of 24.99 and 6.67% (w/w), respectively. It was also studied as a substrate for semi-solid fermentation for the production of highly concentrated glucose syrup through the cultivation of an industrial Aspergillus awamori strain able to produce amylases and cellulases [[35\]](#page-10-0). The use of sugar syrups obtained from waste could be used for ethanol production, reducing waste material created from the cassava starch industry and lowering the cost of ethanol production [[36\]](#page-10-0). Based on this concept, EMBRAPA Food Technology in Brazil [\[37](#page-10-0)] is leading the project ''Ethanol production for fuel cell using residues form the cassava industry''.

Cassava bagasse, due to its rich organic nature and low ash content, can serve as an ideal substrate for microbial processes for the production of value-added products. Attempts have been made to produce several products, such as organic acids, flavor and aroma compounds, and mushrooms from cassava bagasse. Solid-state fermentation (SSF) has been mostly employed for the bioconversion processes [\[38](#page-10-0), [39](#page-10-0)] compared to the fruity aroma production by Ceratocystis fimbriata in solid cultures from cassava bagasse. A strain of yeast Kluyveromyces marxianus was used for the production of a fruity aroma in SSF using cassava bagasse as the substrate [[40\]](#page-10-0).

Because of its high starch content, cassava bagasse was also studied as a solid substrate for the cultivation of edible fungi. The cultivation of Rhizopus strains capable of attacking raw cassava starch showed a yield coefficient between consumed starch and synthesized protein around 0.50 [[41\]](#page-10-0). Several groups studied this residue as a substrate

for mushroom cultivation [[42,](#page-10-0) [43](#page-10-0)], claiming good results for increasing the use of cassava bagasse for animal feed. In addition many authors [[44–50\]](#page-10-0) studied citric acid and fumaric acid production, respectively, using cassava bagasse previously subjected to enzymatic hydrolysis. Fumaric acid has a wide range of applications as acidulant in the food and pharmaceutical industries. Cassava is a major raw material used in many industries in Thailand where it is used to produce monosodium glutamate and other amino acids, sweeteners and ethanol.

In comparison to sugarcane bagasse, cassava bagasse is favored for cultivation of microorganisms because of its well-balanced nutritional composition and that pretreatment is not required. Therefore, production of microbial enzymes could be an area to be exploited using cassava bagasse. Development of efficient microbial strains, mainly fungal cultures, suitable for its bioconversion is still a largely unexplored area. Efforts should be also made to improve the bagasse hydrolysis conditions; moreover, its effective conversion into fermentable sugars needs further research and development.

The use of different chemically modified cassava biomass wastes for the enhancement of the adsorption of three metal ions Cd, Cu and Zn from aqueous solution is reported in literature. The adsorption rates were rapid and about 60–80% of these metal ions were removed from the solutions by the biomass. The binding capacity study showed that cassava waste, which is a serious environmental nuisance due the foul odor released during decomposition, has the ability to adsorb trace metals from solutions [[51\]](#page-10-0).

Wheat and Rice

Wheat was brought to Brazil in the 16th century by Portuguese colonizers. Nevertheless, the first crops were cultivated in the São Paulo Estate after they were moved to the Estates of Rio Grande do Sul and Paraná, currently responsible for 90% of the Brazilian production, where the climate and soil are more appropriate [\[37](#page-10-0)].

The United States, Canada, Australia, the EU-27, the former Soviet Union (including three major wheat exporters: Russia, Ukraine, and Kazakhstan), and Argentina account for about 90% of the world wheat exports, and the US is the world's leading wheat exporter [[52\]](#page-10-0). However, the United Kingdom is losing self-sufficiency in wheat for the first time in its history [\[53](#page-10-0)].

After corn and cassava, wheat is the third starchy crop in Brazil most used as food or feed. In 2007, Brazil produced 4.1 million tons of wheat over an area of 1.8 Mha [\[2](#page-9-0)]. Production and planted areas increased 46.8 and 30.9%, respectively, in 2009, accounting for the production of 6.02 million tons of wheat over 2.4 Mha [[54\]](#page-10-0).

The main residue from the wheat crop is wheat straw (composition of 41% glucan, 19% xylan, 18% of lignin and 7.2% ash) corresponding to 50% of the plant weight. However, the residue from flour production is wheat bran, consisting of 13.5 g arabinose, 22.8 g xylose and 16.7 g glucose per 100 g of starch-free bran [[55\]](#page-10-0).

From the Brazilian wheat production, the wheat crops generate around 6 million tons of straw. Considering that 50% of the straw residues would be available for conversion, over 600 million liters of ethanol and 1 million tons of lignin could potentially be produced. Currently, there is 1.354 million tons of wheat bran annually produced in Brazil, which corresponds to 23% of the wheat production (Table 4). Besides ethanol production, there is also great interest in butanol production from wheat straw. Recently Dupont (U.S.) and British Petroleum announced plans to commercialize butanol from wheat biomass [\[5](#page-9-0), [55](#page-10-0)].

Wheat is still mostly considered a food crop, although 1.2 million tons of wheat will be converted to 450 million gallons of ethanol per year in a large ethanol plant starting to operate in 2010. The plant is located in Teesside, northeast England and belongs to the Carlyle Group and Riverstone Holdings, and the wheat ethanol will be sold to Royal Dutch Shell [\[53](#page-10-0)].

The current world rice production is estimated to be 659.591 million tons, with Brazil being responsible for over 10 million tons, for the most part in the Estate of Rio Grande do Sul that is responsible for over 50% of the rice harvest. The percentage of straw (stem or stalk of rice) in the total plant biomass ranges from 31.2 to 63.9% [[56\]](#page-10-0). As such, 5 million tons of rice straw, consisting of 37% cellulose, 24% hemicellulose and 14% lignin, are produced yearly in Brazil. A unique feature of rice straw is its high silica content, which can be up to 18%. Farmers tend to randomly burn the surplus rice straw, which is not used as compost for soil fertility, directly on the fields as the most economical method of disposal. This practice does not only generate smoke, but also breathable dust that contains crystalline silica and other hazardous substances. However, growers are looking at different ways of disposing off the rice residue in the field, in hopes of developing this "waste" into a potential resource. As such, the utilization of this residue for the production of renewable energy is high on the environmental agenda. Nevertheless, only a

Table 4 Estimated production of residues (wet biomass) from wheat in Brazil in 2008 [\[10\]](#page-9-0)

Raw material	Production (1000 ton)	Residues Amount	of residues (%)	Production of residues (1000 ton)
Wheat Total	5886	Bran	23	1354 1354

small part of the electric energy produced from biomass in Brazil comes from rice waste (9 MW), although the current estimated maximum potential is 200 MW. However, considering that only half of this potential could be profitable due to economic features and transport difficulties, the use of rice straw would allow for the production of 100 MW. Another residue, the rice husk, which corresponds to 23% of the rice volume, presents an oven-dry solid with a percentage composition of 34.4% cellulose, 16.2% xylan, 1.3% arabinan and 23.0% Klason lignin. Similar to rice straw, rice husk has been put to use within the industrial sector for electricity generation. Among the crop residues, rice husk stands out for its highest ash content upon burning. Therefore, researchers have identified new uses for the recovered silica, which can be made into bricks, ceramic articles, and glassware, thus completing the recovery cycle. After burning, these materials can also be used as fertilizer or as raw material for foundry.

Citrus

Citrus fruits crops are the most abundant in the world, producing over 117 million tons of oranges, lemons, grapefruits and mandarins. One-third of the crop is industrialized, with oranges accounting for approximately 82% of the total citrus crop. Citrus fruits are processed mainly to obtain juice; they are also used in the canning industry to produce marmalade and by the chemical industry to extract flavonoids and essential oils. The US is the major individual citrus-producing country, followed by Brazil, which produced 20.767 million tons of citrus fruit in 2008 [\[57](#page-10-0), [58](#page-10-0)].

The solid residues of citrus processing, approximately 50% of the original whole fruit mass after citrus processing for juice, consist primarily of the peel (exterior yellow peel—epicarp plus the interior white spongy peel—mesocarp), membranes and seeds. This raw wet residue contains 76–82% water, 5–8% single sugars (e.g. fructose, glucose and sucrose), 3–5% pectin, 2–3% cellulose, 2–3% hemicelluloses, 1–2% flavonoids, 1% organic acids, 1% protein, 1% ash and 1% oil. The drying process of the citrus residues is hindered by its high $D(+)$ -limonene content as the volatilization of this compound causes air pollution. The limonene vapors exhausted to the atmosphere at the processing plants require expensive equipment to trap it from the drier exhaust [\[59](#page-10-0)]. Nevertheless, taking into account its water content and the aforementioned composition, the dehydrated residue would consist of approximately 31% sugars, 19% pectin, 12% cellulose, 12% hemicellulose, 7% flavonoids, 4,8% organic acids, 4,8% protein, 4,8% ash, and 4,8% oil. However, different data have also reported (in % of dry weight) for the peel and pulp as 9.6 and 6.0 for sugar; 37.1 and 24.5 for cellulose; 11.0 and 7.6 for hemicelluloses, respectively [[58\]](#page-10-0).

Citrus waste constitutes a severe environmental problem as its carbohydrate content is highly fermentable. Traditionally, the waste has been disposed off by dumping, which is an environmental hazard. Marketing of the waste as fodder, another major use, requires the waste to be dried, which is a costly process due to the high water content, as mentioned above. In Brazil, the citrus pulp is commercialized mainly as a pellet and is widely used as cattle feed. Furthermore, part of the citrus pellet is exported. The dried orange peel and pulp residues can be used as organic fertilizer provided the physic-chemical soil conditions as well as the waste properties are well known. The amounts and types of waste added to the soil are defined according to the requirements of the plants produced. Citrus waste can also be composted, thus converting it into a value-added commodity without specialized equipment or facilities [\[60](#page-10-0)].

Citrus residues have many other applications, such as a source of fiber, pectin from the mesocarp and flavonoids from the peel. They are used in the production of human food and food supplements, as a binding agent in food technology and fermentation substrate for single-cell protein production, and as silage and mosquito repellant. However, most of these conversions require advanced technology or facilities [[57](#page-10-0), [60](#page-10-0), [61\]](#page-10-0). $R-(+)$ -Limonene, a major constituent of citrus-essential oils, is an important by-product of the citrus industry. This monoterpene is cheap (US \$1–2/kg) and largely available as its production yields 50,000 tons per year [\[62](#page-10-0)]. As such, limonene is an attractive starting material for obtaining higher-value oxygenated derivatives for the food, cosmetic and pharmaceutical industries, such as carvone, carveol, menthol, alpha-terpineol, perillyl alcohol and perillic acid. The two perillic compounds are of pharmaceutical importance as both have been studied as anticancer drugs. Due to its high regio- and enantio-specificity and the use of mild reaction conditions, the biocatalytic conversion of limonene has been extensively pursued. As such, the production of perillic acid as the major bioconversion product and at high yields from limonene has been achieved using the yeast Yarrowia lipolytica [[63\]](#page-10-0).

Citrus-processing residues have a potential use for the production of bioethanol from its sugars and polysaccharide parts [[64\]](#page-10-0). In Silla, Spain, Citrotecno will build an industrial plant for the production of bioethanol from citrus peels using technology developed by the Universidad Politécnica de Valencia [\[65](#page-10-0)]. In addition, in the 1990s, the USDA Citrus Laboratory developed an ethanol production process that used the citrus peel residual sugars and cellulose [\[52](#page-10-0)]. Moreover, FPL Energy is now constructing an ethanol production facility in Florida that will be the first of its kind to produce ethanol from citrus waste [\[66](#page-10-0)]. Considering that Brazil produces 10.384 million tons of wet residue per year (Table 5), corresponding approximately to 2.080 million tons of dry residue, this material could be used to produce 178 million liters of ethanol based on its sugar and polysaccharide content. However, tailormade process development as well as international collaboration would speed up the development of the relevant technology.

Coconut

The coconut industry generates significant quantities of shell and husk residues that are used in Brazil as sources of agricultural substrates and erosion control blankets, as well as in the production of bio-composites, thermal and acoustic insulation, and ecological roofing [[67](#page-11-0)–[69\]](#page-11-0). These residues can also be used for profitable alternatives products, such as fibers, proteins, enzymes and essential oils, pending the establishment of proper recycle mechanisms at production sites and of processing infrastructure [\[70](#page-11-0), [71](#page-11-0)]. The large increase in coconut consumption as well as in the industrialization of coconut water has lead to increased amounts of the industrial residue, corresponding to around 85% of the fruit weight [[72\]](#page-11-0). Table 6 presents the main coconut producers in the world; Brazil, with 2.8 million tons of coconut production in 2007, is the third main producer. Green fruits, the source of coconut water, with an average weight of 2 kg, represent 15% of Brazilian production. As 85% of the total fruit weight becomes residue,

Table 5 Estimated production of residues (wet biomass) from citrus in Brazil in 2008 [\[10\]](#page-9-0)

Raw material	Production (1000 ton)	Residues	Amount of residues (%)	Production of residues (1000 ton)
Citrus (orange) 88%)	20767	Bagasse, peel and seeds	50	10384
Total				10384

Table 6 Main coconut producers in the world, estimated production (in 1.000 ton) [\[1\]](#page-9-0)

Table 7 Estimated production of residues (wet biomass) from green coconut in Brazil in 2007 [[10](#page-9-0)]

Raw material	Production Residues (1000 ton)		Amount of residues (%)	Production of residues (1000 ton)
Green Coconut Total	-566	Husk	85	481 481

it is estimated that the production of residue reached 481.270 tons in 2007 (Table 7).

The use of shell and husk residues as well as the leaves and trunk of coconut trees cut down can also be used as a source of energy. Nevertheless, their industrial use as an energy source implies the reduction of its moisture content. However, biomass gasification and direct combustion of these residues allows for a more efficient energy output. Coconut shell can also be utilized to produce high-quality activated carbon and charcoal by pyrolysis. Briquettes can also be made from coconut waste and used for energetic purposes.

Gramineous Crops

The by-products of tropical grass seed production in Brazil that is left in pasture areas can become commercialized products with intensive agricultural systems, specific cultural practices and specialized equipment. The existence of favorable environmental conditions for seed production, the presence of a dynamic production sector and the availability of cultivars adapted to a wide range of environmental conditions make Brazil the world's largest producer, consumer and exporter of tropical forage seeds. There are large seed production sites in the Brazilian States of Sao Paulo, Minas Gerais, Bahia, Goias, Mato Gosso and Mato Grosso do Sul. The amount of seed straw residue left in the field is large because tropical forage grasses occupy an area over 140.000 ha per year, accumulating over 20 tons of residues per hectare. Thus, it is estimated that annually about 2.8 million tons of lignocellulosic material is left in the field in Brazil. The residues from grass seed production and the biomass of several cultivated gramineous crops, such as Elephant grass, Brachiaria grass, Panicum spp. and Paspalum spp., could be used for energetic purposes.

It is described the potential of breeding to substantially increase the productivity of the 260 million hectares of savannah grassland in South America [\[73](#page-11-0)]. Recent decades have seen a dramatic increase in the use of the introduced grasses of Brachiaria species, particularly in the Brazilian "cerrados" region. Over the past 30 years, more than 70 million ha of native vegetation has been replaced by

pastures for beef production, particularly of Brachiaria and Andropogon species. In seasonally flooded lands, Paspalum atratum is a grass species native to South America that has attracted much research and commercial interest [\[73](#page-11-0)]. Elephant grass (Pennisetum purpureum), a quickly growing tropical energy crop, has only recently captured the interest of large energy consumers and companies after decades of scientific research. It is a cane-like species of grass, brought to Brazil from Africa at least a century ago, and used as cattle fodder. The interest in its possible use for energy production was boosted by its high productivity [\[74](#page-11-0)]. Elephant grass reaches yields ranging from 30 to 40 tons of dried biomass per hectare per year, and can be harvested two to four times a year due to its rapid growth [\[75](#page-11-0)]. The number of elephant grass varieties is estimated to be around 200, so it would be worthwhile to evaluate the potential of individual varieties to grow under different soil and climate conditions. A 10-year research project carried out at Embrapa's Agrobiology R&D Center identified three varieties of elephant grass best suited for energy production due to their high biomass yield without the use of nitrogen fertilizers. The varieties with the highest biomass yields, lowest nutritional requirements, which are inadequate for animal feed, are desirable for the production of energy. Tables 8 and 9 summarize the pasture areas by continent and in Brazil, respectively. Table 10 presents the most important grass species planted in Brazil.

The Brazilian ceramic industry was the first industrial sector to use elephant grass as an energy source. The dried

Table 8 Summary of pasture areas (in 1.000 ha), by continent [[1](#page-9-0)]

	1980	1990	2000
Africa	911110	920374	869.878
Asia	1016148	1126845	1106.060
America	769041	798909	808920
Europe	85578	82756	182344
Oceania	453465	430511	419455
World	3244404	3368403	3442078

Table 9 Summary of pasture areas (in 1000 ha), by region in Brazil [[10](#page-9-0)]

Table 10 Main grass species planted in Brazil (in 1000 ha) [[85](#page-11-0)]

elephant grass can be used directly in furnaces, replacing wood or natural gas. Other processes needing only heat or steam will soon be able to use elephant grass as an alternative fuel [[76\]](#page-11-0). Furthermore, it has potential for lignocellulosic ethanol production [[77\]](#page-11-0).

Forestry

Forestry wastes correspond to the parts of trees not profited for cellulose production, such as tips and branches, which contribute to soil fertility upon degradation. These wastes are by nature heterogeneous in size, composition and structure. According to the Brazilian Forestry Inventory (Inventário Florestal Nacional), small pieces of wood, including tree bark, are the major waste obtained from the forestry industry, corresponding to 71% of the total waste. Sawdust is second, accounting for 22% [[78\]](#page-11-0). Furthermore, major wood loss occurs during the wood processing in the furniture sector. In some cases, up to 80% of a tree is lost between the tree being cut in the forest and the furniture manufacturing.

In Brazil, short-rotation woody crops such as round wood (Eucalyptus and Pinus) yielded 39 million tons (dry matter) in 2005. Their potential production is estimated at 61.4 million tons (dry matter) yr^{-1} on a planted area of 5.4 million ha with an average mean annual increment from 13 to 14.7 t (dry matter) ha⁻¹ yr⁻¹ [[1\]](#page-9-0). Furthermore, 30.9 million tons (dry matter) of woody biomass from native forests was produced in 2005, of which 8.1 million tons (dry matter) were of saw logs, 20.3 million tons (dry matter) of firewood and 2.5 million tons (dry matter) of wood for charcoal. There are no estimates of potential production. Current production of forest residues in Brazil is estimated to be 38.6 million tons (dry matter) yr^{-1} , of which 59% is field residue and 41% is industrial waste. Plantations and native forests contribute 51 and 49%, respectively. Potential production is 52.8 million tons (dry

Table 11 Current forestry materials production in Brazil [[1\]](#page-9-0), [79](#page-11-0)

Feedstock	Reference Current year	production $(1000 \text{ ton yr}^{-1})$ $(1000 \text{ ton yr}^{-1})$	Potential Production
Short rotation woody crops	2005	39000*	61000**
Woody biomass from forest management	2005	31000*	
Forest residues	2006	39000**	53000**

matter) yr^{-1} , of which 63 and 37% is from plantations and native forests, respectively (Table 11) [[79\]](#page-11-0).

Forestry wastes obtained from the correct handling of the reforesting projects may increase the future forest energetic productivity. The energetic potential of the forestry waste in the world was estimated to be 35 EJ/year (10 GW). Much of the waste is obtained from the plants for wood processing, cellulose and paper. In Brazil, the amount of waste from the cellulose and paper industry with no energy profit is estimated at 5 M tons. A large part of the wastes remains in the field, such as the branches and rest of the trunk, after the tree is cut [[80\]](#page-11-0).

Residues from milling operations have been traditionally disposed in low-technology incinerators, such as beehive burners, a practice being rapidly curtailed because of their air emissions.

Part of the electric energy produced from biomass in Brazil comes from wood waste, and the wood industry is not self-sufficient. Indeed, the current maximum potential is estimated at 594 MW for wood waste. Supposing that only 50% of this potential could be profited due to economic features and transport difficulties, only 300 MW could actually be used. If the actual capacity (142 MW) is subtracted, about 160 MW could be profited [[80\]](#page-11-0).

Besides energy generation, the potential uses of this waste include the production of small wood objects, furniture, and sheets. In addition, forestry waste may potentially be used for the production of bioethanol from its polysaccharide parts. The mean composition values (% of dry weight) are 40–50% for cellulose and 20–25% for hemicellulose [\[81](#page-11-0)]. However, the feasibility of using biomass for the production of bio-fuel and energy generation depends on the availability of appropriate harvesting and processing technologies, as well as the ability to harvest remote biomass resources [\[82](#page-11-0)]. Iogen Corporation in Canada has developed a demonstration plant for the conversion of residual wood to ethanol. Another forestry product-based ethanol production plant currently in operation is Tembec, Canada [\[82](#page-11-0)]. Sweden has vast forestry resources, and industrial processes for producing bioethanol from wood and forestry waste are being developed for large-scale commercial application at ETEK's (Etanolteknik AB) R&D pilot plant in Ornskoldsvik. Seven more plants are planned in Sweden in the upcoming years [\[83](#page-11-0)].

Final Remarks

Environmental, political, geographical and social reasons have recently driven the search for the sustainable production of fuels, mainly ethanol, and chemicals, mainly polymers and chemical building blocks. Nevertheless a significant progress has been made since 2000 in both, first and second generation biofuels, data from the International Energy Agency [[2\]](#page-9-0) show that the only biofuel that decreased production costs in the period from 2004 to 2007 was the first generation sugarcane ethanol produced in Brazil. In contrast the ethanol produced from corn in the U.S. and from sugar beet and wheat in the EU experienced increased production costs, mainly associated with the expense of feedstock. As feedstock cost is crucial, agro industrial residues, which are less expensive than conventional agricultural feedstock, could play a central role for the production of fuels and chemicals. Moreover biomass is geographically more evenly distributed than fossil fuels and hence the energy sources will be domestic and provide security of supply. Furthermore the development of new technologies could provide the much needed employment in rural areas. However, the use of these solar-powered, renewable and cheap biomass resources poises a great logistic and technological challenge, still in its infancy.

The different agricultural activities of various countries and regions are boosting the search for regional technological solutions considering a wide range of advantages as well as its technological complexities and challenges. A wide variety of substrates have been considered, from the simplest to the most complex: sugars (from sugarcane, beet, molasses, sorghum and fruits) that can be converted directly into ethanol; starch (from corn, manioc/cassava and wheat); and biomass (mainly from agricultural residues and wood).

Table [12](#page-9-0) compares various cultures in the world and in Brazil and the normalized contribution of agro industrial residues available in Brazil [[1\]](#page-9-0) that are potential biomass resources for fuels and chemicals production. Nevertheless the existence of significant biomass surpluses in different regions of the country, the use of these resources via a biotechnological route implies the development of the necessary pretreatment and biomass hydrolysis steps in an efficient and economical manner. Moreover, while some residues, such as the ones derived from sugarcane, corn and wheat cultures, are better suited for conversion processes, other materials such as the coconut and rice residues may be more appropriate for combustion, pyrolysis or gasification. Moreover, some residues such as the ones generated

Crop	World production (1000 ton)	Production in Brazil (1000 ton)	% Brazilian production
Sugar cane	1590702	549707	34.6
Soya	220533	57857	26.2
Citrus	117382	20981	17.9
Cassava	214515	26541	12.4
Corn	791795	52112	6.6
Coconut	61504	2831	4.6
Rice	659591	11061	1.7
Wheat	605995	4114	0.7

Table 12 Comparison between the world production and Brazilian contribution for different crops [1]

by the manioc culture have been appropriately used as fodder.

Considering that 80 l of first generation ethanol are produced per ton of sugarcane and that a surplus of 36.5 l could be produced from the conversion of sugarcane bagasse and straw, ethanol production could increase to 116.5 l per ton of sugarcane without increasing the planted area, a topic of great environmental importance. Moreover the burning of lignin, a by product of biomass hydrolysis, would generate over 1385 MJ per ton of sugarcane.

According to the foregoing discussion a total amount of 23.7 billion liters of second-generation ethanol could be produced from the sugar cane residues, 4.4 billion liters from corn residues and 0.6 billion liters from wheat residues, annually in Brazil. Considering that the annual production of first generation ethanol amounts 27.5 billion liters [[85\]](#page-11-0), the conversion of the cellulose part from these agricultural residues could increase ethanol production in Brazil over two fold, without increasing the farming area.

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