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Conversion of Lignin to Heat and Power, Chemicals or Fuels into the Transition Energy Strategy

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Abstract

Energy transition toward low carbon, high sustainable and efficient generation and distribution systems will change the supply matrix of the world and create new opportunities but challenges still remain. Energy generation from biomass, or bioenergy, is one of such renewable sources and its use might be generalized in the following years. Bioenergy is a very promising strategy to provide energy not only for mobility but also for onsite places for heat and power generation. Besides, bioenergy differentiates from other renewable energies that biomass may be the source of a myriad of molecules enabling the bio-based economy and allowing the replacement in an extent of solvents, petrochemicals, and polymers produced by the petroleum industry. Biomass is generally composed of some large polymers found in nature such as cellulose, hemicellulose, proteins, starch, chitin, and lignin. The latter is a complex phenylpropanoid biopolymer conferring mechanical strength to plant cell walls and one of major spread in nature along with cellulose and chitin. Lignin has a plenty of potential uses in modern bio-based economy, from conventional paper industry uses to more challenging conversion to useful chemicals, materials, and clean biofuels. This chapter undertakes a rapid overview on lignin applications in order to describe the basis of a lignin-based economy.

Keywords: lignocellulosic materials, lignin, biorefinery, bioeconomy, heat and thermal power, bio-based chemicals, biofuels

1. Introduction

Although the world energy balance is dominated by fossil fuels, one major issue raised is how to change the future energy matrix toward more sustainable and renewable sources of energy.

The inclusion of renewables—wind, solar, geothermal, water and biomass—in the energy matrix has been marginal because of high costs and underdeveloped technologies. However, recognition of the damaging environmental impact from excessive dependence on fossil fuels, along with the growing concerns about the supply of some fossil fuels to meet rising global demand for energy, has brought into focus, the need for a cleaner and more diversified energy mix. Considering the challenges of the twenty-first century, including energy transition toward low carbon, bioenergy plays a key role in the diversification of sources of energy supply. In addition, the use of alternative fuels and bio-based chemicals will be increased to complete the energy matrix.

Biomass can be used directly (e.g., fuel wood for heating and cooking) or indirectly by converting it into a liquid or gaseous fuel (e.g., alcohol from sugar crops or biogas from animal waste). The main biomass processes utilized in the future are expected to be direct combustion of residues and wastes for electricity and heat generation, bioethanol and biodiesel as liquid fuels, and combined heat and power production from energy crops. The future of biomass electricity generation lies in biomass-integrated gasification/gas turbine technology, which offers high-energy conversion efficiencies. Biomass will compete favorably with fossil mass for niches in the chemical feedstock industry [9]. Hence, bioenergy is recognized as the energy derived from the conversion of biomass and where the biomass may be used directly as fuel, or processed into solids, liquids, and gases [16].

Biomass is mainly composed of three macromolecular biopolymers known as cellulose, hemicellulose, and lignin. Cellulose is composed of β -D-glucopyranose units linked by (1-4) glucosidic bonds and different polymorphs has been described from high to amorphous crystallinities [22]. On the other hand, hemicellulose is mostly amorphous and generally classified into four groups: (1) xyloglycans (xylans), (2) mannoglycans (mannans), (3) xyloglucans and (4) mixed-linked β -glucans [12]. They are considered the most abundant biopolymers on superior plants on earth just followed by lignin.

In this chapter, we present the actual and potential contribution of lignin as a source of solid, gas or liquid biofuels but also as a platform for bio-based chemicals and materials.

2. Lignin

Lignin is an amorphous and highly branched polyphenolic polymer with phenylpropane units, which may be present in varying amounts in biomass, comprising around 8–30% of biomass weight (**Table 1**). The complex structure of lignin contains numerous ether linkages, hydroxyl and methoxy groups and, therefore, a high-oxygen content. This cross-linked macromolecule is composed of three types of monolignols or lignin precursors, also known as phenolic monomers, including p-coumaryl, coniferyl and sinapyl alcohol (**Figure 1**). These precursors correspond to the p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units in lignin, respectively [7]. Lignin is considered the glue agent that gives robustness and strength to the cellulose microfibril systems surrounded by hemicellulose [10, 11].

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Calorific value (GJ/ton)	Density of compressed material (kg/m ³)
Wood (<i>Pinus</i> spp.)	43.3	25.9	29.6	18.3	906.8
Agave bagasse (<i>Agave atrovirens</i>)	45.9	26.6	8.7	15.5	868
Sugarcane bagasse (<i>Saccharum officinarum</i>)	32.3	35.2	22.4	19.1	721.7
Corn stubble (<i>Zea mays</i>)	39.1	30.9	18.6	15.6	928.2
Wheat Straw (<i>Triticum</i> spp.)	42.9	28.9	21.6	17.9	899

Table 1. Biomass composition, calorific values and densities of compressed materials [18].

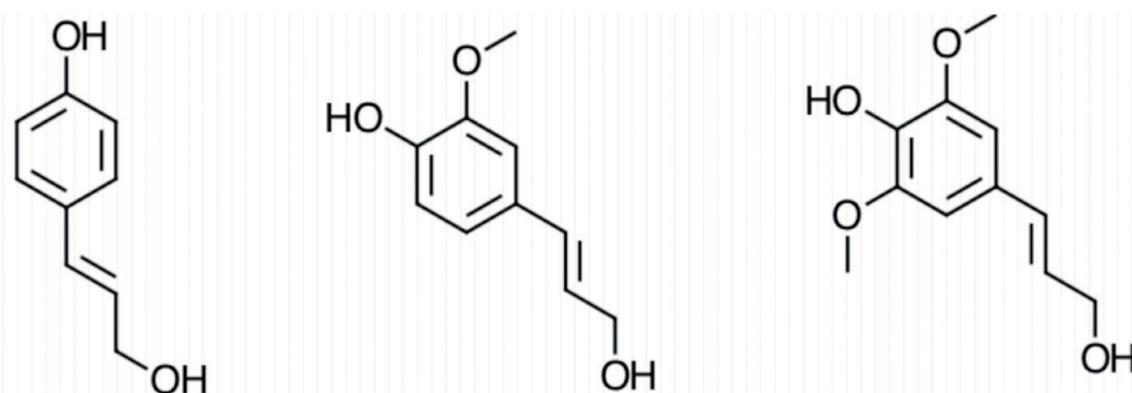


Figure 1. Lignin precursors from left to right: p-coumaryl, coniferyl and sinapyl alcohols.

The main classification of wood includes softwood (gymnosperm as pine or spruce) and hardwood (angiosperm as oak and walnut); the former is usually cheaper than the latter because about 80% of all timber comes from softwood. Softwoods have a wide range of applications and are found in building components (e.g., windows, doors), furniture, medium-density fiberboard (MDF), paper, Christmas trees and so on. Hardwood is usually used in high-quality furniture, decks, flooring and construction that need to have a long life. Lignin present in softwood usually has more coniferyl alcohol (75%) and less p-coumaryl (5%) and sinapyl alcohol content (20%) than that present in hardwood (50, 10 and 40%, respectively; [24]).

Lignin in biomass may be valued through the generation of thermal and electric power as well as the production of materials and chemicals (**Figure 2**). Here, we focus on industrial uses of biomass-containing lignin and processed or extracted lignin. Therefore, we focus on sawmill, agro-industrial and agricultural activities. Concerning forestry activities in sawmills, we refer to FAO definitions. Please keep in mind that there is not sufficient data and mass balance may be not complete. Hence, roundwood refers to all quantities of woods removed from trees inside the forests and from trees outside the forests. It includes all woods removed with or without bark, including woods removed in its round form or split form and considered fuel wood, sawlogs and veneer

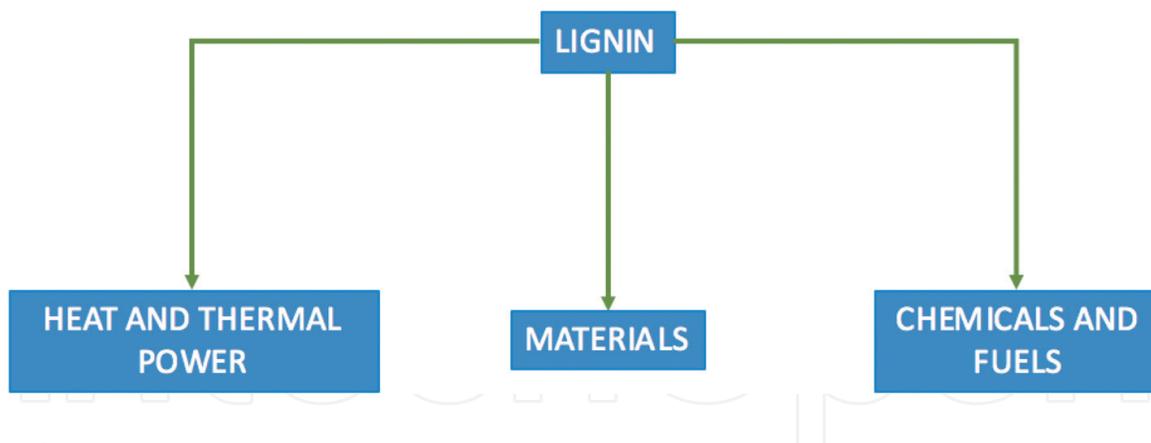


Figure 2. Scheme of lignin uses.

logs, wood pulp, round and split and other industrial roundwood. All fuel wood is roundwood that will be used for cooking, heating or power production, while wood pulp is the fibrous material prepared from pulpwood, wood chips, particles, residues or recovered paper by mechanical and/or chemical processes for the manufacturing of paper and other cellulose products [13].

According to FAO, the world production of industrial roundwood, wood fuel and wood pulp is shown in **Table 2**. This forestry biomass might be considered as the available raw material for processing into power, materials, chemicals and fuels. If we look at specific countries, USA and China lead the potential production of roundwood in coming years (**Figure 3**). Nevertheless, European countries such as France and UK as well as Latin American countries such as Chile and Mexico together represent the potential production of China but with a smaller population.

Regarding regional plant production, *Agave* is a succulent genus belongs to the monocot family Agavaceae [29] and the most important plants in Mexico are *A. tequilana*, *A. angustifolia*, and *A. atrovirens*, which are used for the production of spirit and fermented non-distilled beverages such as Tequila, Mezcal and Pulque, respectively. Agave plants have a lower content of lignin ranging from 7 to 16% [18, 29], and are considered easier to process when compared to wood species (lignin content around 30%) and Gramineae such as cane sugar, corn, wheat (lignin content around 18–22%).

As we mentioned earlier, lignin is the third most abundant biopolymer on earth, when we assess the occurrence on superior plants and it plays an important role in the transition energy global agenda (**Figure 4**). OECD countries, in **Figure 4**, possess an interesting potential of roundwood-derived lignin production that can help to achieve the Paris 21st COP's agreement.

Wood product	World production (thousand m ³)	World production (metric tons)
Roundwood	1.836,541	1,240,906
Wood fuel	1.863.828	1,259,343
Wood pulp	255,930	172,926

Table 2. World production of roundwood, fuel wood and wood pulp [13].

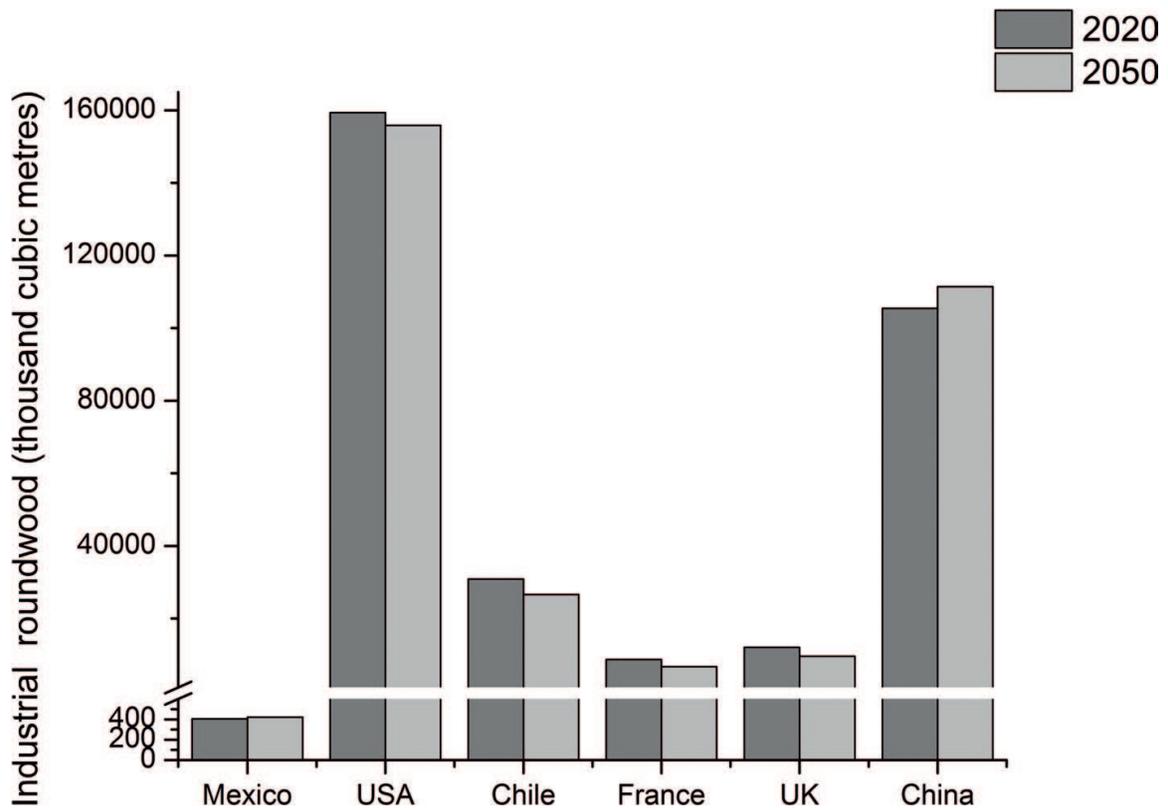


Figure 3. Industrial roundwood potential production in selected countries between 2020 and 2050.

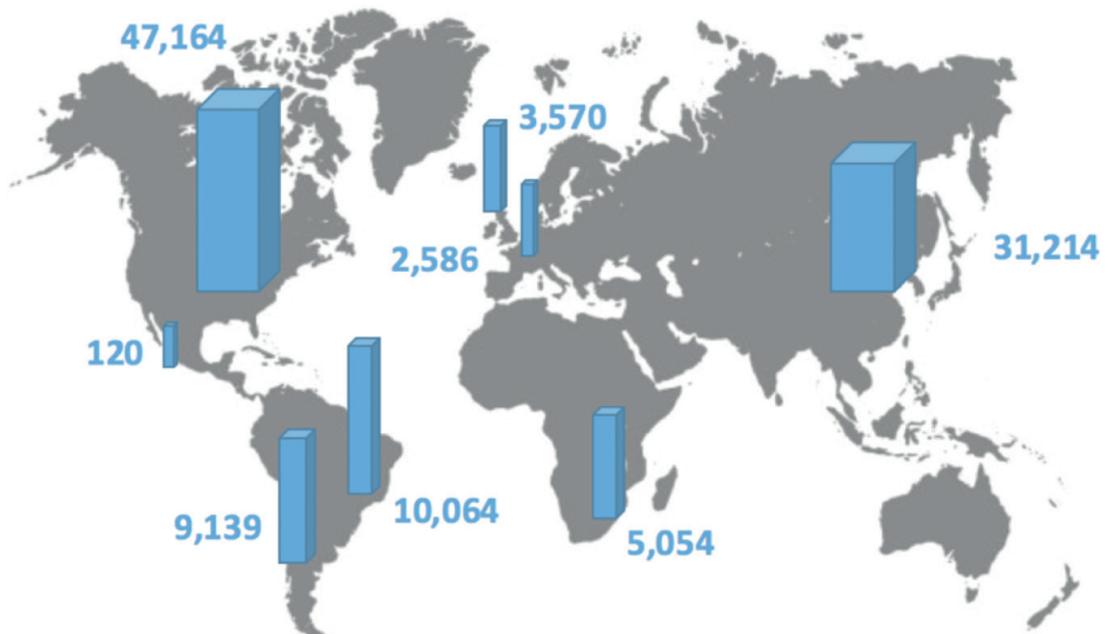


Figure 4. Lignin potential production from roundwood products in selected countries (1000 cubic meters; [13]).

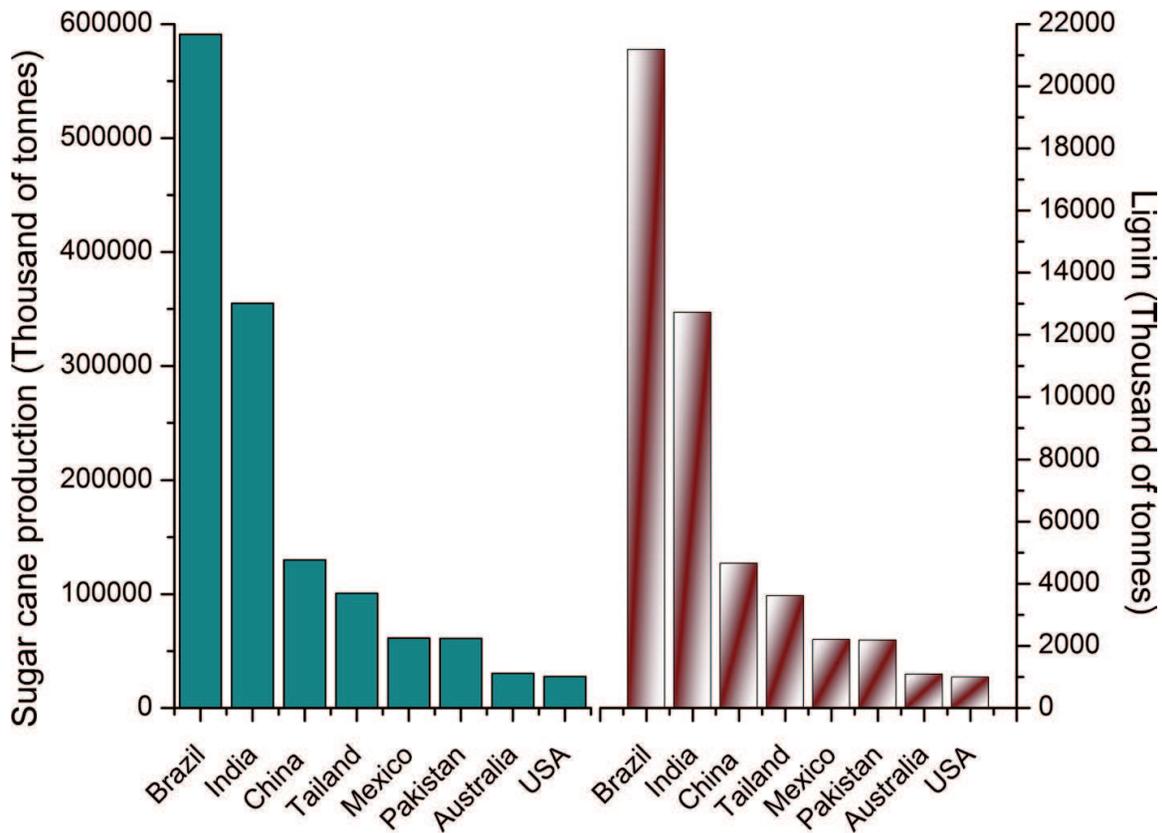


Figure 5. Sugarcane production in selected countries in 2013 and estimation of lignin content based on own data [30].

Sugarcane is another interesting crop since its industrial processing is already done in an integrated biorefinery, where all plant is valued into sugar, molasses, heat and electric power, and in some cases, into ethanol as oxygenated agent in gasoline (Figure 5). Indeed, since the earlier 1970s, countries like Brazil has undergone an intensive program of sugarcane production because there is an enormous need of alternative fuel for gasoline, considering Brazil's dependency of oil and gas importations during that time. Other countries like India, Mexico and, in a lesser extent, the USA produce sugarcane and sugarcane-related products but they also have an important potential of value-added lignin from the bagasse.

Traditional crops such as maize and wheat may be considered as a source of biomass and lignin for energy and chemical production (Figure 6). Their production is spread all around the world but some countries like Mexico has forbidden the use of cereal grains, rich in starch and considered as a cultural value, for energy uses. Nevertheless, we must consider that such biomass already has conventional and important value-added uses in land fertility, erosion mitigation and livestock breeding. The partial use of such biomass may be accompanied with integral policies that protect and assure the quality of renewable soil as well as the mitigation of disturbance on conventional value chains and stakeholders.

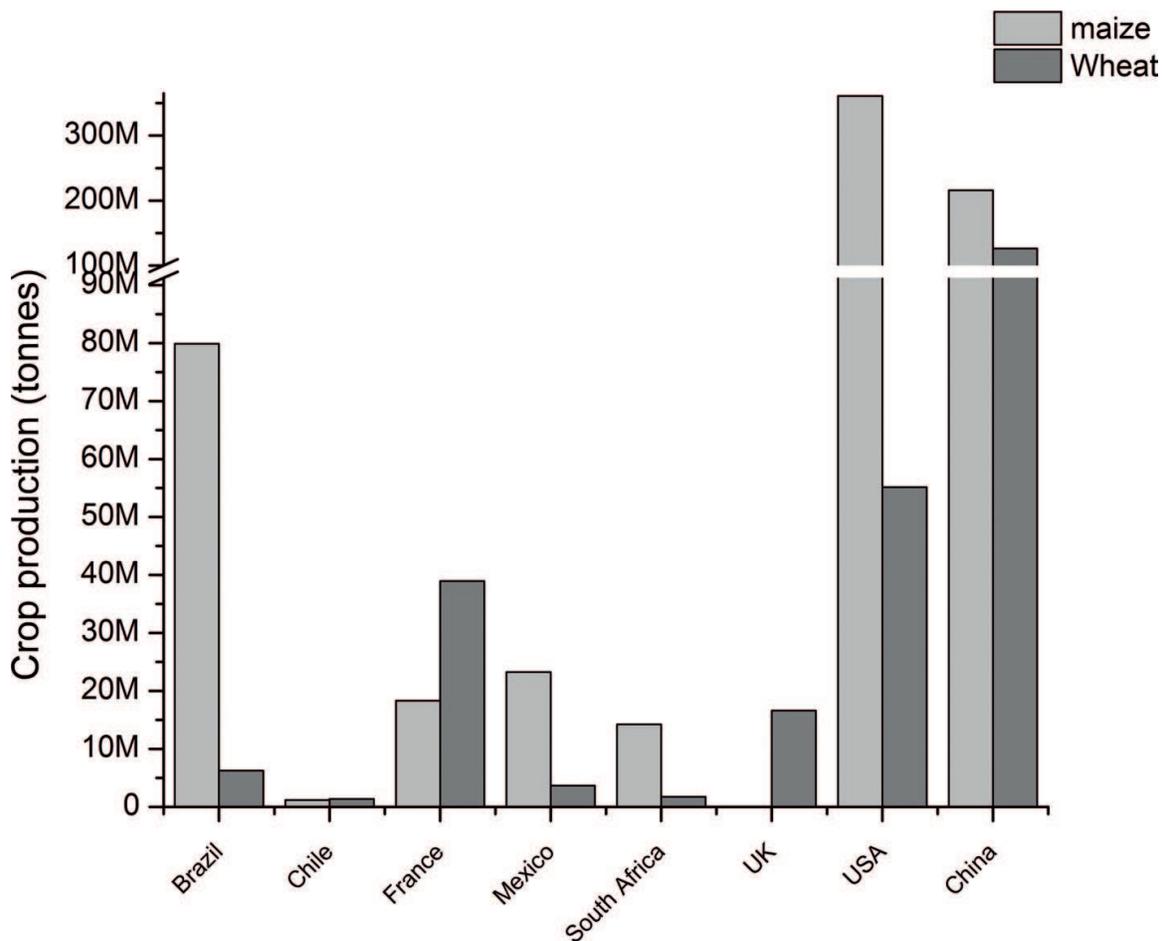


Figure 6. Maize and wheat production in selected countries in 2014 [13].

3. Generation of heat and power

According to the Chemical Sciences Roundtable of the National Research Council [21], burning biomass to produce energy and heat is nothing new, but doing so at a large scale still cannot economically compete with coal and natural gas. Local, small-scale biomass-to-power systems may prove to be the most efficient way of generating energy from biomass. Already, small-scale production of biogas from biomass and on-site co-generation of electricity and heat is widespread in Europe. Farm-sized units are in operation in the United States as well. One interesting example is sugarcane-producing mills which find its residue, sugarcane bagasse, a reliable and affordable source of thermal and power generation for auto-consumption needs with an installed capacity between 10 and 50 MW. Sugarcane has 16% of fiber or bagasse (dry basis) with almost 9% of lignin ([1, 6, 18]; see Figure 5). Then, we estimated the potential energy supply considering a caloric value of 19.1 GJ/ton for sugarcane bagasse (see Table 1 and Figure 7). We obtained for Mexico, a 188 PJ/year potential energy from sugarcane bagasse, which is lower but within the range reported by IRENA and REMBIO (Bioenergy Mexican Network in Spanish; [15]).

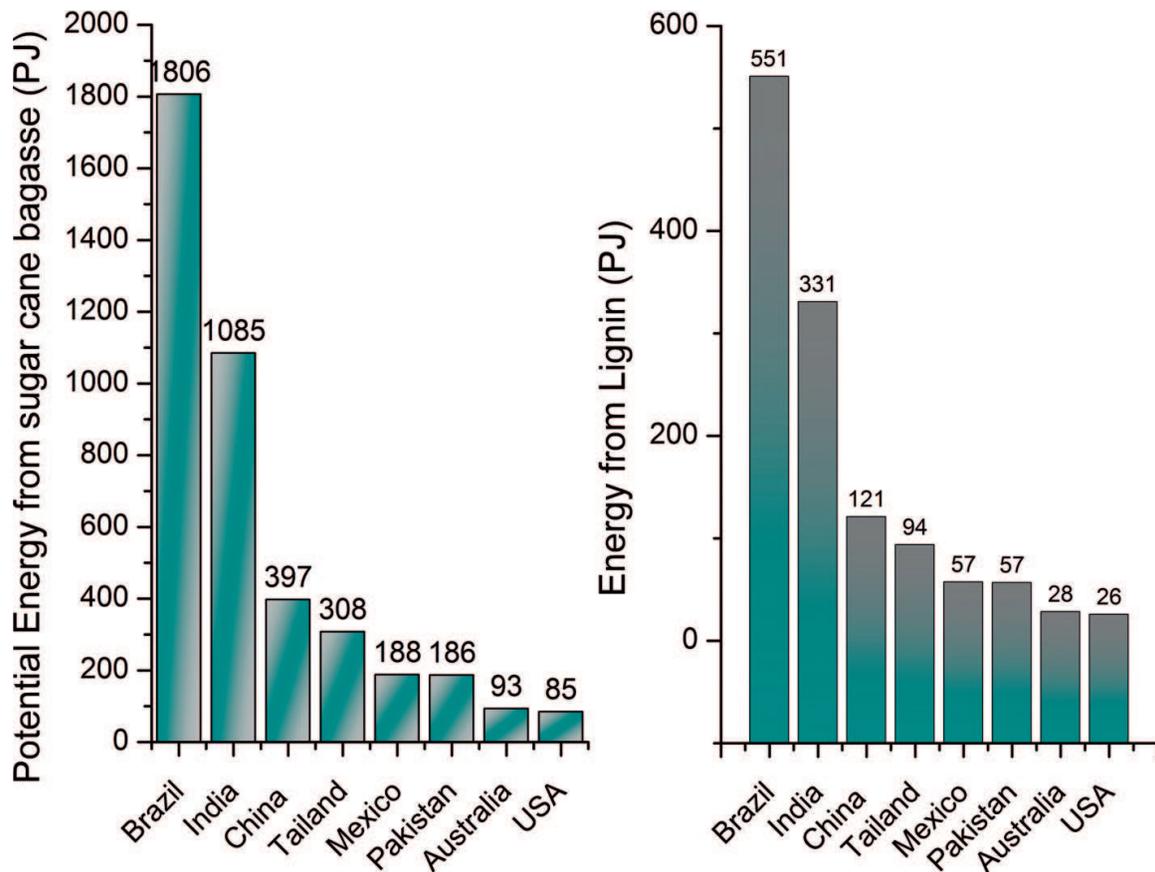


Figure 7. Potential energy from sugarcane bagasse and its isolated lignin in main producing countries.

In developing countries such as Mexico, Chile and even China, the predominant fuel in rural areas is still wood fuel from forest clearing and recollection (**Figure 8**), but traditional generation of heat for cooking through open fires or stoves generates a lot of smoke, carbon black, has low conversion efficiencies with 10–20%, and biomass is often sourced unsustainably. On the other hand, industrialized countries have developed more sophisticated forms as pellets and bricks produced from wood processing industries [20].

Nowadays, the biomass feedstock can be quite different depending on regional or international distribution for specific needs and consumptions like residential (<0.5 MW) to medium (0.5–10 MW) and large plant power capacities (>10 MW; **Table 3**). According to International Energy Agency (IEA) [16], residential thermal generation as well as medium and large power generation with biomass is already economic and environmental competitive with other fuels such as coal and natural gas.

Indeed, renewable energies for heat and power generation are increasingly competing with fossil fuels since the reduction of capex and opex costs altogether with their better performance, even without government subsidies but carbon tax implementation might accelerate their adoption. Many factors affect the capital cost for renewable project including market, government policy, technology availability and maturity and capacity factors such as scale size. Solar photovoltaic and wind are considered as raw feedstock, free in contrast with the heat and power generation from biomass where its availability, logistics, conditioning, quality/volume, regulatory issues

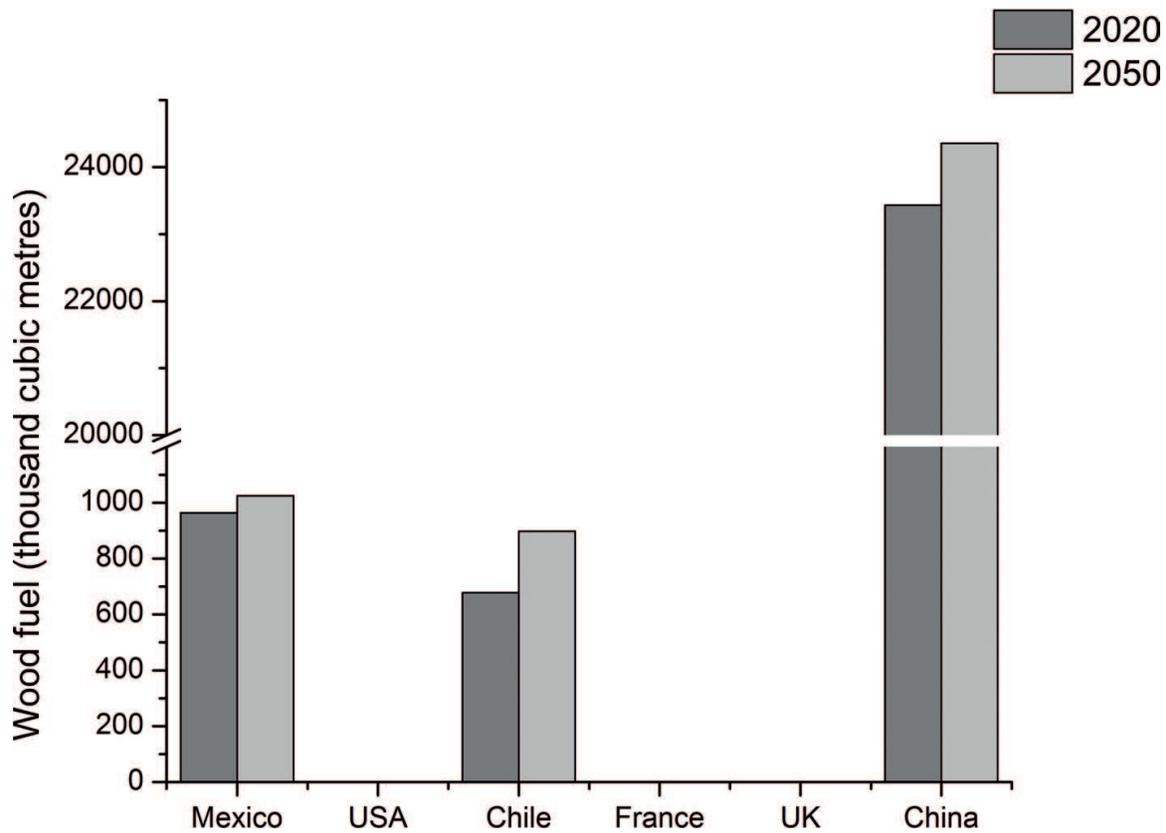


Figure 8. Wood fuel potential production in selected countries between 2020 and 2050.

	Biomass			
	Wastes	Processing residues	Locally collected feedstocks	Internationally traded feedstocks
	Organic waste, sewage sludge, manure	Timber residues, black liquor, bagasse, rice husk	Agricultural residues, roundwood, energy crops	Roundwood, wood chips, biomass pellets, biomethane
Feedstock costs (USD/GJ)	<0	0–4	4–8	8–12
Plant capacity	0.5–50	0.5–50	10–50	50
Typical power generation efficiency (%)	14–18	14–18	18–33	28–40
Capex (USD/kW)	6000–9800	6000–9800	3900–5800	2400–4200

Table 3. Some biomass feedstocks to produce power and heat, and related costs [16].

among others affect its cost as energy source. These costs may hugely vary depending also on scale and country, but some weighted costs show that all three technologies may compete on the field but government policy must assure equal conditions based on competitiveness (Figure 9). We observed that biomass is one of the more competitive alternatives for power generation in all world regions in contrast with fossil fuels and other renewable energies, but usually the lack of

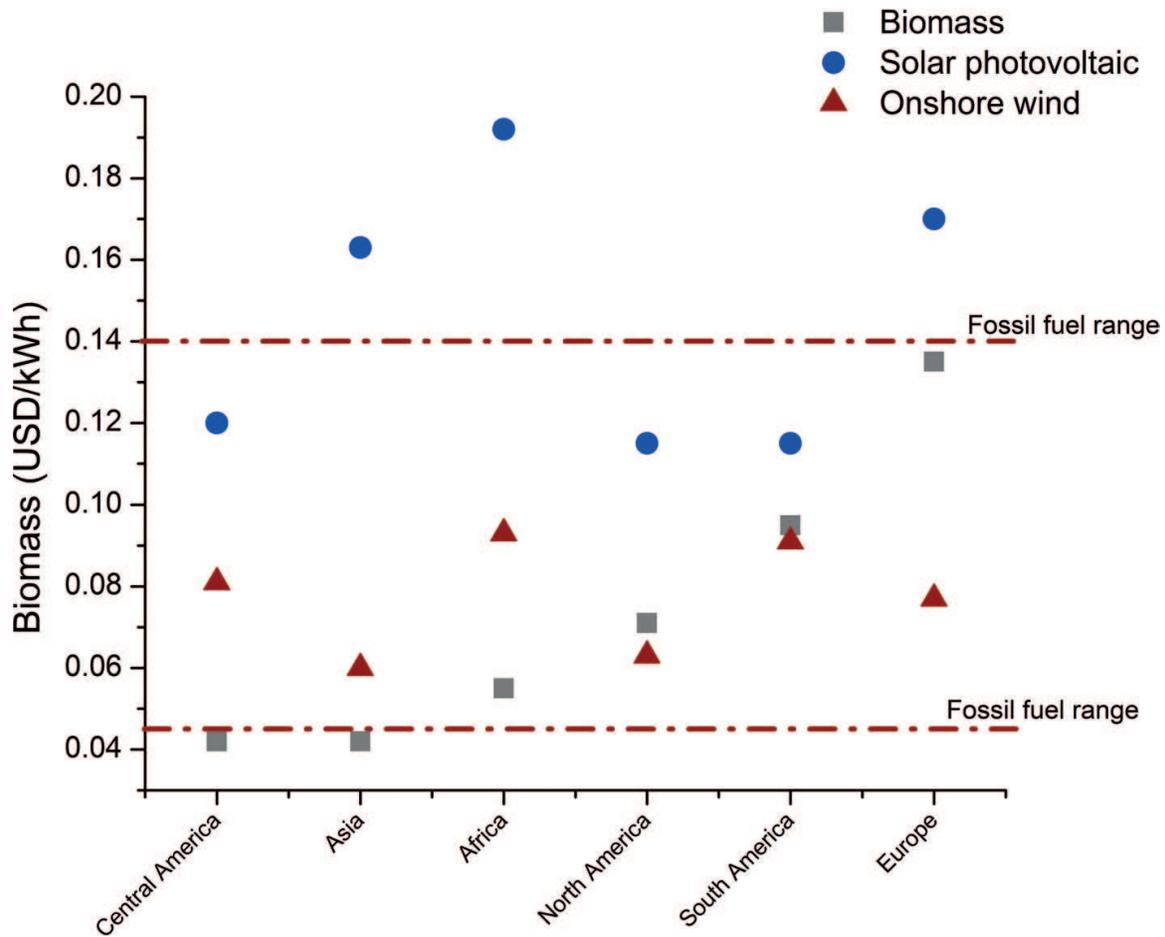


Figure 9. Weighted average cost of electricity (USD/kWh) by world regions and compared with fossil fuel power generation costs [15, 16].

an affordable and reliable source of biomass, related with social issues, may increase considerable associated risk, which makes the credits and the biomass costs more expensive. Wood- and lignin-based biomass might play an important role in the generation of sustainable heat and power, but they are needed policies that help to transit on this sinuous road.

4. Chemicals and fuels

Lignin as a polymeric material and pulping wood derivative has followed the development of paper industry all around the world since the end of nineteenth century. In such industry, lignin must be separated in order to get access to the more valuable cellulose. Hence, the alkali and acidic procedures are the more expanded method in industry and they allow obtaining of lignin derivatives such as alkali, kraft, liginosulfonate and organosolv lignin, respectively (**Figure 10**). An effective method to separate lignin is the organosolv process, which uses alcohol mixtures with water at high temperature near 200°C, sometimes with the aid of an alkali or acid in order to improve the lignin removal and wood pulp quality. Today, by far Kraft lignin dominates the market over liginosulfonate and organosolv lignin with a 90% share.

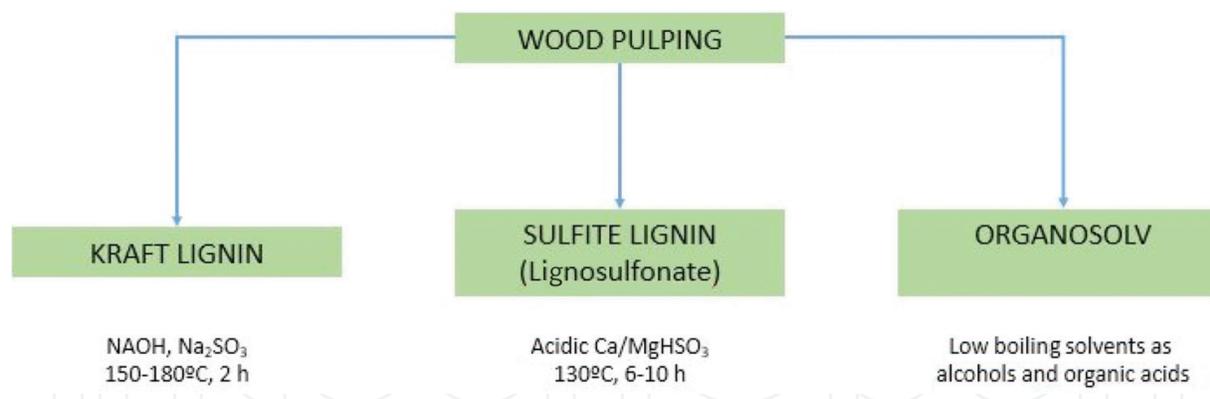


Figure 10. Scheme of conventional production of lignin derivatives in paper industry.

Kraft lignin is used in oil refineries as carbon crackers, cement additive and production of biofuels, BTX and other specialty chemicals such as vanillin and phenols. Lignosulfonate chemical is used in textile industries, thanks to its water solubility and functional properties as binders, dispersants, emulsifying and complexing agents. Nevertheless, the need for a sulfur-free agent is reconsidering lignosulfonate market hegemony for cleaner and sustainable sources of lignin [5].

Lignin may also be recovered by solubilizing the recalcitrant crystalline cellulose and amorphous hemicellulose using chemical, thermochemical, biological and/or enzymatic approaches [3, 7, 19, 23, 25]. We have recently developed a mixed chemical-enzymatic pretreatment of lignocellulosics to solubilize almost all cellulose and hemicellulose, except a lignin-rich polymer as seen by FTIR analysis (**Figure 11**). Indeed, we can see the empty cells where cellulose used to be leaving an interesting hole material with infrared characteristic signals at $4000\text{--}2500\text{ cm}^{-1}$ $\nu\text{O--H}$, $1700\text{--}1740\text{ cm}^{-1}$ $\nu\text{C=O}$ carbonyl and carboxylic groups, $1590\text{--}1610\text{ cm}^{-1}$ $\nu\text{C=C}$ aromatic skeletal and 1126 cm^{-1} $\nu\text{C--O--C}$ ether groups.

Here, lignin might be the source of materials, energy, biofuels or bio-based chemicals but we may consider two routes to achieve this: (1) its conditioning to obtain materials or bioenergy and (2) its depolymerization followed by conversion to polymers, fuels or bulk or fine chemicals (**Figure 12**). The simplest approach considers a biorefinery where lignin may serve as an energy source through direct combustion, gasification or pyrolysis, as discussed later in the section, but also for the production of materials such as activated carbon and/or biochar [8, 14].

Indeed, biochar production during pyrolysis of biomass or the fraction of lignin must be considered in an integrated biorefinery, where it helps for the economy and environmental impact of the whole process. Additional studies are needed in order to quantify the carbon capture by soil and microbes, reduction of CO_2 emissions due to bio-oil displacement of fossil fuels and decreased use of fertilizers, as well as reduction of NO_x emission from soils by better soil aeration [5, 17].

The present and future transition into a less depending fossil fuels economy needs not only renewable energy but also renewable raw materials like biomass and lignin to satisfy the need for materials and chemicals used in our everyday life. Biomass is the only renewable source known today that may support not only the generation of heat and electric power but also the processing and manufacturing of fuels and goods. Solar energy also has indeed the potential to achieve this; it does every day in leaves, algae and microorganisms such as microalgae and cyanobacteria [2]. Nevertheless, its development is still incipient but full of encouraging challenges.

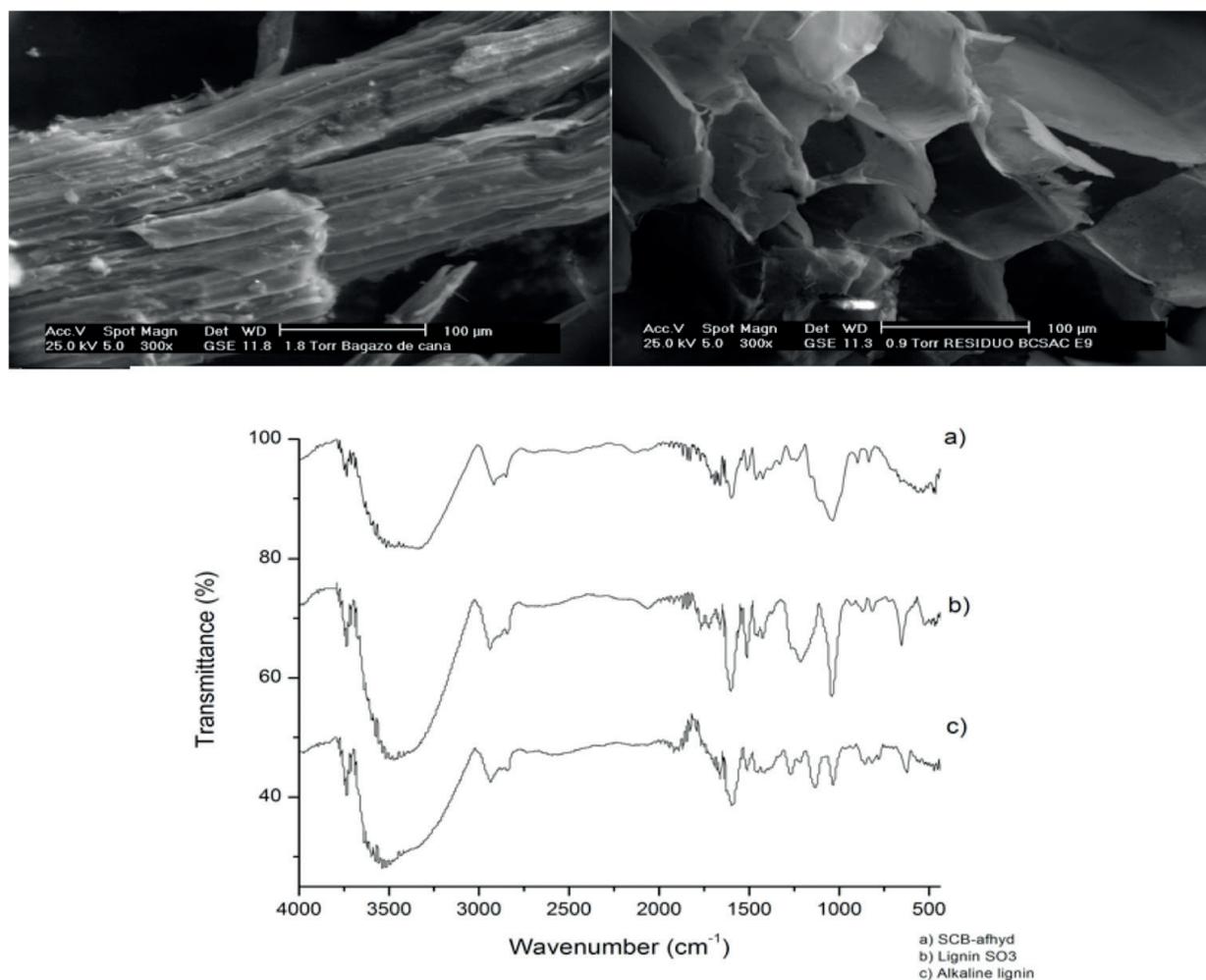


Figure 11. Scanning electronic micrographs of sugarcane bagasse before (top left) and after (top right) chemical and enzymatic pretreatment. FTIR spectra of pretreated (a) sugarcane bagasse, (b) liginosulfonate lignin and (c) alkali lignin.

A modern and integrated biorefinery will process low-value biomass into energy for self-consumption and export excess to the grid. More valuable biomass may be used for the production of edible or nonedible oils, protein-rich flour for fish/shrimp farms and used to convert the lignocellulosics into fuels and chemicals [4]. We have identified four additional market niches for lignin derivatives: (1) conventional paper-related derivatives; (2) specialized chemicals; (3) commodity chemicals; and (4) biofuels (Table 4). The first two have already established markets since low value-added generic industrials to high value-added flavor and fragrance additives. The latter use has a high demanding worldwide market for aromatic and phenol-based compounds that may be obtained from lignin. This approach must be considered in a biorefinery scheme since their high price may account for the financial sustainability and competitiveness of the business. Indeed, the flavor and fragrance industry may reconsider inverting the balance between the use of aromatic compounds from fossil source against biomass or lignin raw materials, that is, compounds like phenylacetic acid, benzoates, phenylacetates, cinnamates, phenols, phenyl esters, alcohols and ethers, among many others [27].

In present and near future terms, biorefineries must be additionally considered to balance the production of biofuels and chemicals that can be used without any or less change in current



Figure 12. Scheme of conventional and potential products from lignin. BTX: benzene, toluene and xylene isomers and DMSO: dimethyl sulfoxide.

Market niches	Lignin derivative	Market volume (Mtons/year)	Price (USD/ton)
Conventional paper related derivatives	Lignosulfonates	1,000,000	350
	Kraft lignin	100,000	364
	Organosolv lignin	1000	919
Specialized chemicals	Lignin-based vanillin	3200	1200
	Crude oil-based vanillin	12,800	1200
	Natural vanillin	60	600,000
Commodity chemicals	BTX	102	1200
	Phenol	8	1500
Biofuels and fuels	Bio-jet fuel-based on lignin/ biomass	1–50% in mix with fossil jet fuel	1300–6400
	Fossil oil-based jet fuel	252,456	400

Table 4. Market volumes (Mtons) and price (USD/tons) of some conventional and emerging chemicals and fuels [26].

established technologies, known as drop-in fuels and chemicals. In this sense, lignin as a source of chemical compounds such as benzene, toluene, and xylenes might be relevant today to some petrochemical platforms but the demand is insignificant related to other higher volume markets as biofuels or specialized chemicals. Additionally, environmental and health issues will certainly become more stringent in near future, limiting the use of such compounds. Nevertheless, the society will need more advanced chemicals, building units, and materials, and lignin may be a reliable and sustainable source of new upcoming technology platforms.

Lignin-based biofuels may be obtained basically from three routes: (1) hydrothermal depolymerization and excess oxygen elimination; (2) slow or fast pyrolysis to depolymerize the lignin into a bio-oil that must be processed to eliminate excess of oxygen, and (3) gasification followed by biomass to liquids (BTL) process or Fischer-Tropsch process for the obtention of different fuel fractions or even alcohols [3, 28]. Even if these technologies represent the today and near future options to satisfy the need for clean, sustainable and neutral carbon fuels; the real issue is the deployment of such technologies and their spread adoption in order to comply with the world weather change commitments.

5. Final remarks

Lignin is a versatile polyphenol raw material comporting a significant presence in biomass. Due to its chemical nature, it is difficult to isolate and process into chemical commodities, specialized chemicals, thermal and/or electric power and also advanced biofuels. The actual energy transition requires a significant change of paradigm between the past unsustainable fossil energy source to more advanced environmental, health and socially committed sources of reliable, renewable and sustainable forms of energy; among those, bioenergy from biomass and lignin will play an important role. As a part of biomass, lignin has plenty of potential uses in a modern bio-based economy, from conventional paper products to more challenging processes such as its conversion to useful chemicals, materials, and clean biofuels in a biorefinery scheme.

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