



TOPICAL REVIEW

Lignin-based carbon fiber: a current overview

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TOPICAL REVIEW

Lignin-based carbon fiber: a current overview

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4 July 2018Felipe Souto^{1,3} , Veronica Calado¹ and Nei Pereira Jr²¹ School of Chemistry, Federal University of Rio de Janeiro, Department of Chemical Engineering, Rio de Janeiro, Brazil² School of Chemistry, Federal University of Rio de Janeiro, Department of Biochemical Engineering, Rio de Janeiro, Brazil³ Author to whom any correspondence should be addressed.E-mail: fsouto@eq.ufrj.br, calado@eq.ufrj.br and nei@eq.ufrj.br**Keywords:** carbon fiber, lignin, composite, biomaterial, structure, renewable**Abstract**

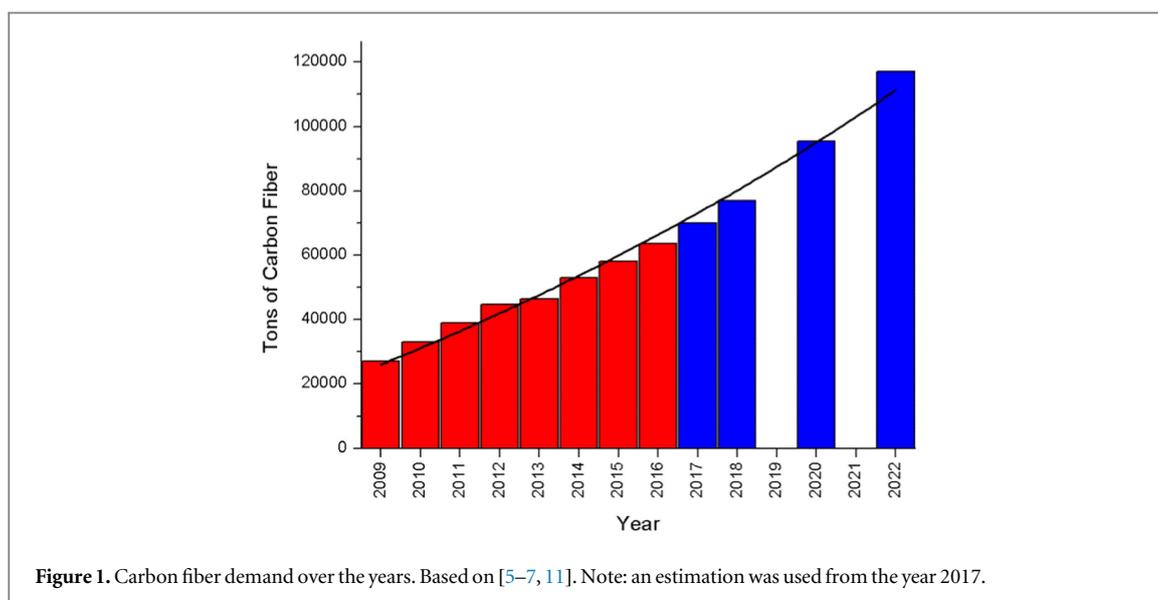
Research involving lignin use is not new. For many years, the macromolecule was underestimated in its potential and burned for energy use in pulp and paper industries. However, with the advent of biorefinery on the valorization of lignocellulosic fractions, lignin is receiving greater motivation to be researched. Of the many applications, the most profitable one is its conversion into carbon fiber. Lignin-based carbon fibers can reduce the manufacturing price of this fiber to values greater than 35%, besides using a renewable material with a highly sustainable appellation. This paper gives an overview about lignin-based carbon fiber comparing the process to current precursors, presenting different pathways on different research, pointing to the most common difficulties and assessing new findings. A gap not fully clarified yet is concerning the lignin structure and its relation to extrusion process. After isolation procedures, lignin repolymerizes in a different manner compared to when it is in its natural form. Some studies have shown that some organic functions, the molecular weight and the structure conformation of the lignin can favor or disfavor thermal mobility. Although it is known purification is considered a criterion that favors extrusion, there is no study involving a selection of parameters that improves thermal mobility. Herein, it is highlighted a set of desired structure properties that provides a very good thermal mobility and extrusion in order to obtain a lignin-based carbon fiber with good properties.

1. Introduction

Market demand for carbon fibers has grown dramatically in recent years and the reasons are justified by their unique and attractive mechanical properties. Compared to steel, carbon fibers are ten times stronger and five times lighter; and compared to aluminum, it is eight times stronger and 1.5 times lighter. They are flexible and heat resistant, biologically inert and they also have low thermal expansion and low density [1–4]. Because of their unique properties, its use covers many sectors of applications: civil engineering, aircraft and aerospace, automotive, molding and compound, wind turbines, sports and leisure, marine, pressure vessels, oil and off-shore drilling, etc.

Carbon fiber demand increased from 26,500 tons in 2009 to 63,500 tons in 2016, which yields a revenue up around US\$ 2.34 billion (a growth of 8.7% related to the year 2015). According to market trends (figure 1), it is expected an annual growth rate between 10% to 13% for the coming years [5–7].

Polyacrylonitrile (PAN) is the major precursor used in the manufacturing process of the fiber and it is responsible for about 51% of its cost [8]. The material yield, the toxicity of the solvent, and the costly manufacturing steps are factors that encourage searching for substitutes more viable, technically and economically [9]. Another precursor widely used is pitch, even though mechanical properties are lower compared to PAN-based. PAN and pitch are of fossil origin. As more economically viable substitutes emerge, some by-products and natural or synthetic residual products have been studied. Therefore, it is crucial for this new raw material to be an organic product with a high carbon content; the final yield of the precursor might give at least 10% (wt.) of material; and it must not become liquid or tacky during carbonization [10].



A renewable resource component with high potential to produce carbon fiber is lignin. It competes with chitin for the second position of most abundant organic macromolecule in nature [12]. Lignin is present in all vascular vegetables and it has a high carbon content ($\approx 60\%$ carbon content) and wide availability [13, 14].

Pulp and paper industries process, annually, around 50–60 million tons of lignin [15], and about 98% is intended for energy use by combustion and the rest is isolated and recovered for some commercial applications [16, 17], such as pesticides [18, 19], cement and concrete [20–22], animal feed [23, 24], emulsifier [25, 26], water treatment [27–29], and so on. However, evidence has shown that these applications, primarily combustion, remain an underuse of the macromolecule.

Furthermore, lignin extraction tends to increase worldwide, demanding research that gives the best value for lignin use. Based on that, some successful attempts to convert lignin into carbon fiber were obtained providing significant results of its viability and effectiveness. Moreover, preliminary estimates have demonstrated that this purpose is the most economically and energetically advantageous application for the macromolecule [30]. If lignin were implemented in the carbon fiber sector, its profitable use would be about 2000 times higher compared to burning. This fact would add value of around US\$ 800 000/fiber ton to the lignin [30].

Lignin-based carbon fiber has emerged as a material with high technological impact, economically attractive, and environmentally sustainable, although it is still far from being competitive with current precursors, showing signs of becoming a viable substitute for certain application areas, mainly those of the low-cost segment of the market, but with high demand.

This paper gives an overview on lignin-based carbon fiber manufacturing. More than comparing earlier articles in the literature, it discusses relevant issues on the topic based on current knowledge. Although lignin conversion into carbon fiber is not new, the attempt to use neat lignin is only possible in special conditions and it still provides a fiber with restricted mechanical properties. Some studies have identified some chemical linkages that favor thermal mobility. Notwithstanding, there are no studies using this knowledge to select the set of structure conditions to extrude the lignin. Herein, the matter of the lignin conformation is discussed and commented on with this purpose. Moreover, the molecular weight distribution develops an important factor on the extrusion procedure; however, little is known about the correct range to be obtained. On the manufacturing, some comments over the processing temperature are provided alerting to some unrestricted vices commonly applied. This is due to the misguided application of using the reference temperature of standard precursors on lignin. Lignin-based carbon fiber is, nowadays, a reality but it still needs some processing improvements. This paper comments on some common obstacles, presenting and providing information from the beginning of the research to the present.

2. Lignin

Responsible for a weight of 3×10^{11} tons in biosphere, lignin (together with chitin) is the second most abundant material in nature, after cellulose [31]. With an increase of an annual rate of 2×10^{10} tons, 30% of all carbon atoms in nature are from lignin [32].

The origin of its name comes from the Latin *lignum* which means wood and its structure is present in the cell wall of all vascularized vegetals, with cellulose and hemicellulose [33, 34]. During the last decades, lignin

structure was cited as tridimensional, complex, heteropolymeric, amorphous, crosslinked and branched chain [35, 36]. Recent research has suggested that in its natural form (protolignin), its molecular framework may be predominately linear, composed mostly of β -O-4 intermolecular bonds (45%–84% of occurrence) [35–37]. It can be considered a hydrophobic macromolecule, irregularly constituted by phenylpropane units with methoxyl and hydroxyl groups [38].

This new linearity concept of lignin has been evaluated over the years. Nowadays, it is known that the biosynthesis of the protolignin is governed by relative prevalence of monolignols, transport and diffusion of monomers to cell wall and physical weathering [37]. The lignification process, thus, is conducted by peroxidase and laccase enzymes, building the protolignin structure [37]. For many years, the models of Freudenberg (1964) and Adler (1977) were used [39, 40]. In their models, the lignin was accepted as an irregular polymer, with a tridimensional arrangement. But in 2003, after analyzing the structure of wheat straw with chemical ionization in tandem with mass spectrometry and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, Banoub and Delmas (2003) suggested, for the first time, a linear model structure for lignin [40, 41]. The new model was not totally disseminated, even though molecular simulation studies have suggested a helical structure (spiral conformation) for β -O-4', β - β' and β -5' linkages [42]. However, current studies focused their interests on β -O-4' linkage, promoting a synthetic lignin structure [43, 44]. Based on NMR and Mass Spectroscopy analysis, they realized the linear feature of these linkages [44–47]. The β - β' and β -5' bonds also showed linear structures by the analysis [45, 46]. As cited, once lignin is mainly formed by β -O-4' linkages, this suggests that its structure is more likely to be linear than branched. While there is still no conclusive result over these cited theories, the structure of the lignin still needs further investigation for further recognition. Table 1 shows the main linkages that compose the lignin structure and figure 2 presents a comparison between a possible linear model and a tridimensional model (Freudenberg model) of the lignin.

Among many functions, lignin is responsible for nutrients and metabolites transportation; mechanical resistance assigning rigidity to the plant; protection of tissue against microorganisms and weather; and so on [33, 48]. Therefore, as plants are submitted to different biological and chemical weathering, the protection function of the lignin models its structure according to necessity and its biotype. This justifies why there are distinct structures found in different species and families of plants, or even in different parts of the plant of the same species, or from different cultivation regions. According to its structure, lignin presents different physicochemical properties.

Three subunits are randomly repeated forming the lignin structure: p-hydroxyphenil (H), guaiacyl (G) and syringyl (S). They are results of the dehydrogenation of alcohols coumaric, coniferyl and sinapic, respectively [49]. Generally, softwoods are more homogeneous structurally, with H:G:S ratio around 4:95:1. That means that it is more concentrated in guaiacyl subunit. In contrast, hardwoods and grass are more heterogeneous, presenting H:G:S ratios around 1:25:25 and 1:14:5, respectively [50]. Based on that, softwoods are known to have what is called guaiacyl lignins (guaiacyl subunits greater than 90%), while hardwoods and grass are called syringyl lignins [51].

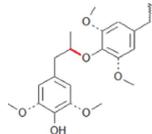
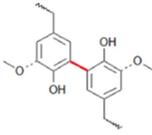
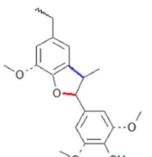
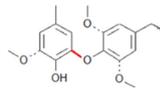
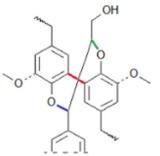
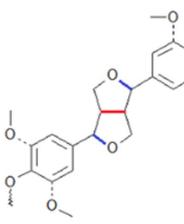
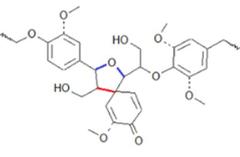
Figure 3 presents the structure of lignocellulosic materials that are formed by cellulose, hemicellulose and lignin.

2.1. Extraction methods and their influences

Many extraction methods have been used to isolate lignin from the vegetal, but not one allows for obtaining it in its native form (protolignin) [33, 52]. This is because of the different ways that each method cleaves the lignin structure in lignocellulosic complex [53]. Depending on the isolation process, the cleavage can occur in different sites of the chain, fragmenting the lignin in different molecular weights [54]. Competitively, these fragments can repolymerize during the reaction step, forming carbon-carbon bounds in condensation reactions [36, 55, 56]. These condensed structures are more recrudescant and hard to cleave.

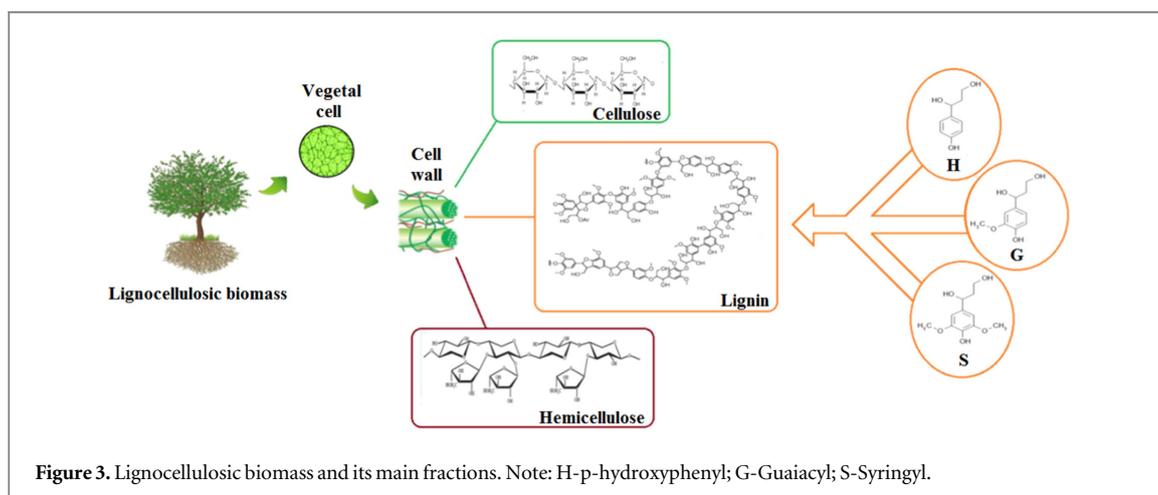
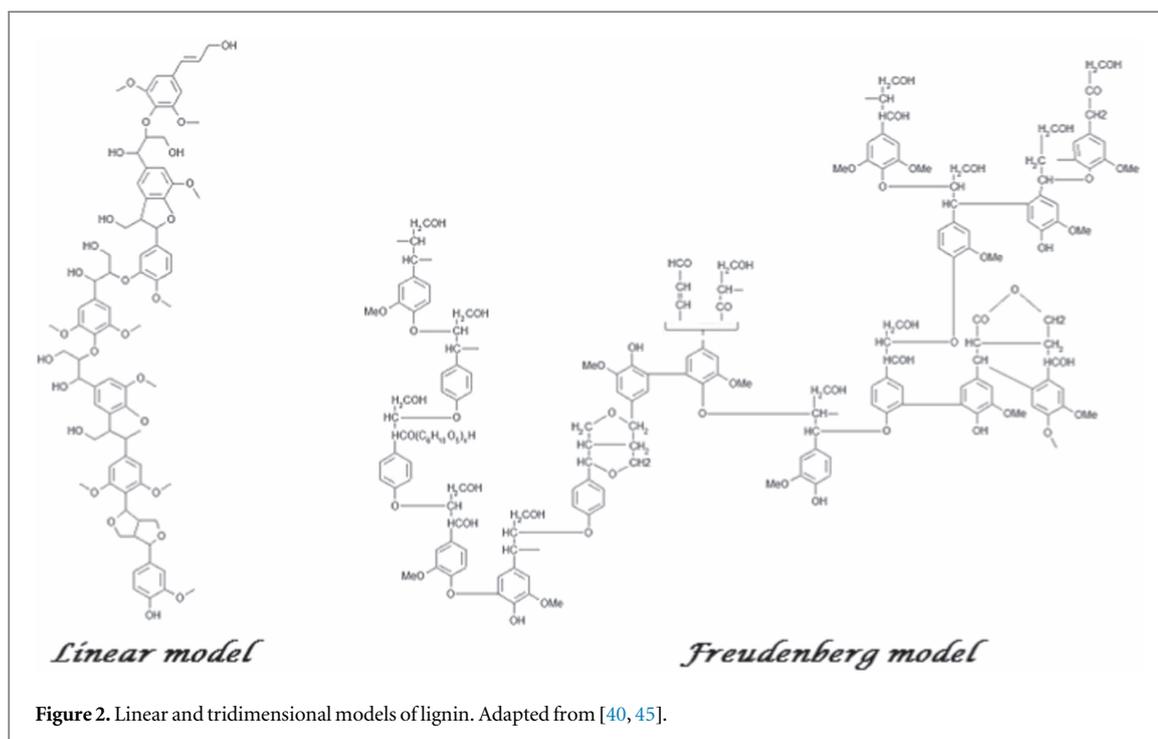
All those factors, coupled with the diversity of possible structures mentioned, molecular weight, pressure, contaminants, thermal history and cross linking justify in each case why lignin has unique physicochemical properties [57]. Therefore, lignin has no specific glass transition temperature, for example; it will depend on the structure set formed after the isolation procedure [57]. Once recovered from the extraction method, lignin presents a completely different structure compared to protolignin, where it is commonly called technical lignin [58, 59]. That suggests that depending on the vegetal, the part of the vegetal, its origin, its age, the isolation method and the recovery process, technical lignin will have a unique structure with particular properties. This interrelationship between structure and properties still needs further evidence. For example, alkaline processes attack or disrupt ether bonds, like β -O-4' [35, 37, 60]. These bonds are the majority on the structure of the protolignin and lately studies suggested that they are responsible for the linearity on the macromolecule, together with β -5' and β - β' linkages [46]. Once cleaved, competitive condensed reactions can occur, rearranging the lignin with C-C linkages that are more likely to be tridimensional [61–64]. Thus, a hypothesis is that the

Table 1. Main lignin linkages and their frequencies. Based on [37].

	Softwood (%)	Hardwood (%)	Non-Woody (%)
 Arylether (β-O-4')	45–50	60–62	74–84
 Biphenyl (δ-δ')	<9	4.5	n.d.
 Phenyl coumarin (α-O-4' + β-5')	9–12	3–11	5–11
 Diarylether (δ-O-4')	2	2	n.d.
 Dibenzodioxocin (δ-5' + α-O-4' + β-O-4')	5–7	<1	n.d.
 Resinol (β-β' + α-O-γ')	2–6	3–12	1–7
 Spirodienone (β-1' + α-O-α')	1–9	1–7	n.d.

n.d.-non-detectable.

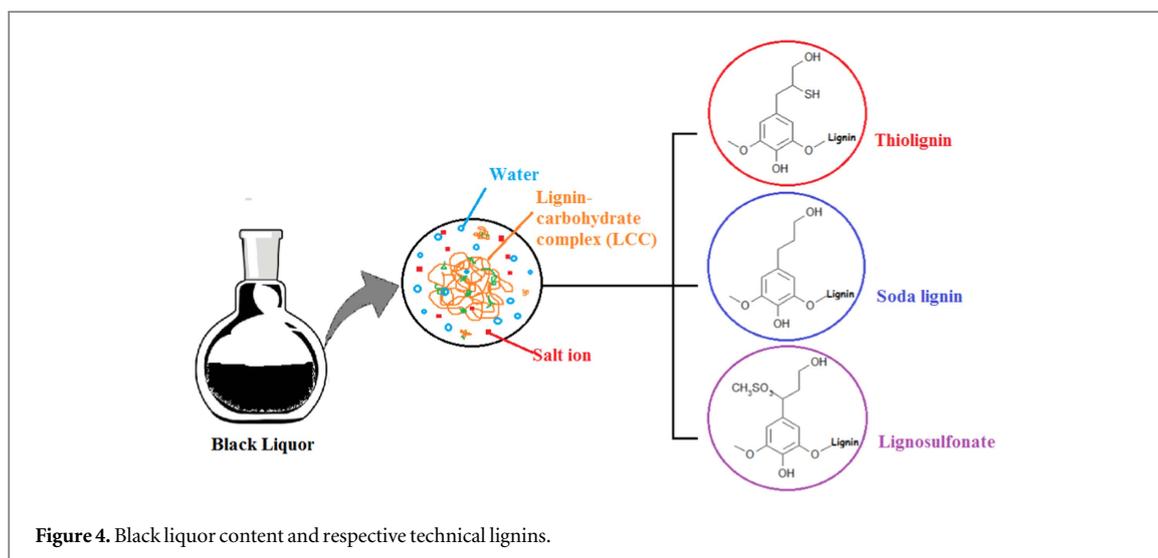
Note: According to Rinaldi *et al* (2016), biphenyl is rarely found in free form; it is more common to find its occurrence in dibenzodioxocin structure; β -1' does not exceed 1%–2% of all structures [37].



technical lignin presents a tridimensional arrangement instead of the protolignin. When the word lignin is mistakenly used for protolignin and technical lignin, one can get confused with the real feature of the structure conformation. The issue still requires further investigation.

Among all methods available to extract lignin, Kraft or sulfate process (providing a technical lignin called thiolignin), sulfite process (providing liginosulphonates) and soda process (providing soda-lignin), are the most employed. They are greatly used in pulp and paper industries, where the Kraft process stands out for being the most used worldwide, corresponding to about 85% of all lignin removed during the pulping process [65]. Generally, Kraft and sulfite processes are performed on woody feedstock, while soda process is more properly applied to fibrous material [66]. The Kraft process, among the others, has the advantage of providing a greater yield of lignin, but with the incapability to provide a lignin chemically bounded with sulfur in its structure, as the sulfite process does. Soda process, although a milder process, provides a sulfur-free lignin, but with a lower extraction yield [67].

Both Kraft and soda processes cook the vegetal feedstock in an alkaline medium (called white liquor), with the difference that in the Kraft process, an addition of Na_2S is provided. The obtained products in the vegetal digestion are called Kraft black liquor and soda black liquor, respectively, where lignin is dissolved [66]. Herein, the liquors are named to distinguish the process from which they came, although, technically black liquor is commonly used without any designation. The sulfite process, differing from the others, cooks the vegetal feedstock with a mixture of sulfite or bisulfite salts with sulfurous acid [68]. The diagram in figure 4 presents a



'black liquor' content and a possible technical lignin subunit from each recovery process. Note that in thioglignin and lignosulfonate structures, sulfur is organically bounded. Thioglignin presents an insertion of sulfur that can reach up to 3%, while lignosulfonates can reach up to 8% [65].

Some impurities can be found with technical lignin all over these processes. Carbohydrates are generally present reaching between 2% to 8% of contamination, depending on the extraction/recovery process [69, 70] Hemicellulose is the main carbohydrate present. Because of its strong covalent bond with lignin, it is hard to separate them completely [4, 71]. There is little evidence of linkages with cellulose [72]. Therefore, many authors refer to these technical lignins as a lignin-carbohydrate complex (LCC) when it is hard to obtain a neat macromolecule [73–75]. Casually, linked to these polysaccharides, some recalcitrant amino acids from the feedstock might be found [58, 76]. Presence of some particulate matter can be attributed to sand, diatoms, clay, and vegetal fibers [77]. Inorganic compounds can also be present in a form of salts, and water molecules can chemically be bounded with phenolic hydroxyls [78]. All these highlighted materials can be considered contaminants in which, depending on the extraction process, can be evidence compared to the other.

Worldwide, over 1.3 billion tons of weak black liquor (15%–20% of dry contents) are annually produced or the equivalent of about 170–200 million tons of black liquor dry solids [79–82]. An evaluation indicated that around 130 million tons (measured as dry solids) come from Kraft pulp [37]. From this amount, about 40 million tons per year can be extracted from Kraft mills with no adverse effect on mill balance [83]. Therefore, these industries generally burn this excess to sell the energy generated.

The MeadWestVaco Co., the world's largest producer of Kraft lignin, started recovering technical Kraft lignin from the black liquor in 1942, and in 2011 it was the only factory in the world selling commercially technical lignin [84, 85]. Later, in order to provide a technical Kraft lignin with less impurities, Innventia and Chalmers University Technology developed, together, a process (Lignoboost[®]) that reduces ash content and carbohydrate presence during its recuperation. The technology was sold to Metso Co. FP Innovation, in Canada, who also developed a recovering process (Lignoforce[®]) with low ashes, low carbohydrate and low sulfur content. The GreenValue, in Switzerland, also provides non-wood technical soda lignin in commercial scale with low impurity contents [86].

The number of lignin commercial suppliers increased recently once the material was thought to have a different potential. However, for high-value application, some purity is required, and that is why many technologies have been developed. Lignosulphonates are also available in high commercial scale, although their high amount of impurities makes them a source for low-value use [30, 86].

Another process that has been prioritized in biorefineries is the Organosolv. Technical lignin provided by this method is more preserved and sulfur-free (it uses organic solvents), and it has been tested in pilot scale in Canada (Lignol Innovations Ltd, producing HP-L lignins), in France (CIMV, producing Bioglignin) and Germany (Dechema/Fraunhofer) [30, 86].

The Organosolv process was first introduced as an alternative to replace Kraft and sulfite processes, with the appeal of avoiding malodorous emission (sulfur free), to be environmentally friendly, with an efficient and simple chemical recovery system, with the capacity of extracting mostly lignin (low loss of cellulose and hemicellulose), to provide a high quality/purity lignin (low content of carbohydrate and ash), etc [87]. Generally, the solvents used can be either low-boiling-easily recovered by distillation-(e.g. acetone, methanol, ethanol, propanol) or high-boiling-useful at low pressure-(e.g. ethyleneglycol, ethanolamine) [88]. The solvents

can be used alone or in an aqueous medium, with or without addition of a catalyst. It has a promising use in biorefinery because it produces a cellulosic pulp with a good enzymatic digestibility and allows for a clean fractionation of cellulose, hemicellulose and lignin [89]. The first study using organic solvents to fractionate wood components was in 1893, using ethanol and hydrochloric acid [90]. In the late 1960s, research on the process intensified [37]. In 1992, there were two plants operating at full scale (Organocell and ASAM), and two others testing as pilot scale (Acetosolv and Milox) [87]. Nowadays, besides Lignol, CIMV and Dechema cited above, several studies focused on the use of THF-water (tetrahydrofuran) and GVL-water (γ -valerolactone) co-solvents have been introduced. The increasing use of these two aqueous solvents is due to its capability to partially solubilize/decrystallize crystalline cellulose to sugar platform valorization [91]. Organosolv activity and research have grown greatly over the past 50 years [37] and with the advent of the biorefineries, it is expected its application will increase over the years.

3. Carbon fiber

Carbon fiber is hugely applicable as an engineering material and it has been used as reinforcement in polymer-matrix composites owing to its high modulus and tensile strength [92]. Around 98% of all carbon fiber production are applied to composite materials [30]. Some authors assume that this fiber contains up to 90% of carbon in its structure [93], while others are more restrictive to limit a range of 92% to 99% of carbon in its constitution [94, 95]. The diameter of its filaments measures 5 to 15 μm , depending on the manufacturing procedure or the precursor used [94].

Carbon fibers are extensively used in composites and can be applied in many areas in which the precursor type and manufacturing process are critical. Comparatively, carbon fiber composites are more expensive than metals, albeit they are becoming more competitive and cost effective [96]. For many years, these materials were mostly used for aerospace, given their high performance and limitation imposed by their high price. But in recent decades, the demand has increased considerably and their use can be found in aerospace, sporting goods, prostheses, construction, automobile, pressure vessels, drilling risers, turbine, textile machinery, etc. Even with this worldwide increment consumption of carbon fiber composites (CFC), they are still too expensive. Reasons are related to the costs of manufacturing the fibers and the composite. CFC prices could be reduced by increasing processing volume; cheapening carbon fiber price; providing high performance resins meeting production automation requirements; reaching cost effective product forms; and so on [96]. As the processing volume has increased and the technology of the composites has unleashed, some alternatives have been invested in order to lower the price of the fiber as a possible solution.

The first carbon fiber obtained by Thomas Edison (1880) was the carbonization product of bamboo to manufacture a filament for the lamp [97]. Later, in 1958, Roger Bacon manufactured carbon fibers based on Rayon, at the Union Carbide Parma Technical Center (now GrafTech International) [98]. Around the year 1960, Shindo used PAN for high-performance carbon fiber for the first time [99]. Nowadays, PAN and pitch are mainly used commercially. PAN ranks in first position in the market because it provides the best mechanical properties for the final material [3, 100, 101]. Rayon lost market position because of its inferior properties and low yield [102]. Research using new precursors is widely overdeveloped nowadays and can be basically divided into four types [93]:

- (a) Acrylic-mostly used, which is (acrylonitrile monomer)-based (approximately within 85%), e.g. PAN;
- (b) Cellulosic-more complicated, which provides low carbon yield (25%–30%), e.g. Rayon;
- (c) Pitch-based-provides high carbon yield (85%), high modulus fiber and low transversal and compression properties;
- (d) Others-Vinylidene chloride, phenolic resins, lignin, etc, are being studied as raw materials.

Carbon fibers can be classified by their mechanical properties (tensile strength, tensile modulus and elongation), precursor, and thermal treatment. Based on that, different applications can be employed. Generally, these classifications are interconnected. For example, some properties can only be reached if the precursor used allows for such capacity. But even using an appropriate precursor, an adequate heat treatment is necessary in order to achieve the desired property. The set of properties are important to define the area of application. Table 2 combines classifications and types of carbon fibers. Producers generally use mechanical properties to classify their material [103]. It is important to mention that, despite not employed on table 2, diameter and morphology are also an important criteria to classify the fibers when it confers important prominence on mechanical properties [103].

Table 2. Classification and types of the carbon fibers. Based on [30, 104].

	Types	Values (GPa)
Based on fiber properties	Ultra-high modulus	600–965
	High modulus	345–600
	Intermediate modulus	275–345
	Standard modulus	200–275
	Low modulus	40–200
	High-tensile	>3.0
	Super high-tensile	>4.5
	Types	Subtypes
Based on precursors	PAN-based fiber	—
	Pitch-based fiber	Mesophase/Isotropic
	Rayon-based fiber	—
	Lignin-based fiber	—
	Types	Temperature/Classification
Based on heat treatment	High heat treatment	>2000 °C/high modulus
	Intermediate heat treatment	Around or above 1500 °C/high-strength
	Low heat treatment	Around 1000 °C/low modulus and strength

Note: Precursors are not restricted on PAN, Pitch, Rayon and lignin.

3.1. Carbon fiber manufacturing

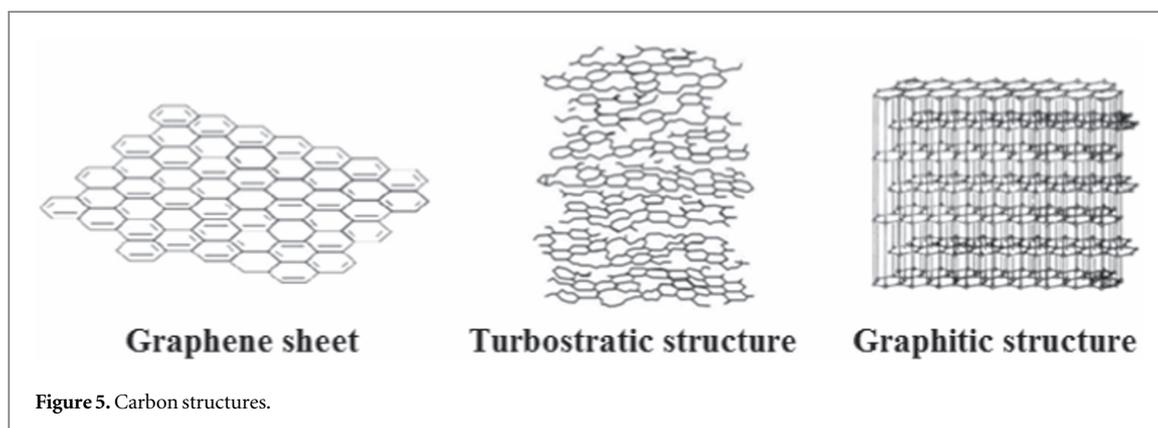
Carbon fiber is commonly manufactured by the following steps: extrusion/spinning, oxidation or thermostabilization, carbonization, graphitization, surface treatment and sizing [30].

The most applied spinning techniques are melt spinning, melt assisted spinning, dry spinning, wet spinning, dry-jet spinning, melt-blown spinning and electrospinning [30]. The choice of method depends on the operability conditions of the raw material. For example, for materials whose degradation temperature is near the fusion temperature, the most appropriate options are wet spinning and dry spinning over the melt spinning [105].

After spinning, the as-spun fibers generally need a thermostabilization step. It is the most expensive step of the manufacturing process; it consumes energy and takes a long time to execute. That is why optimization research is being developed [106]. This step is important to ensure infusibility of the material during the subsequent step (carbonization), where the fiber is no longer a thermoplastic and becomes a thermoset-type [107]. The oxidation of the fiber should be performed slowly so as not to compromise the material structure while performing the appropriate increase in its glass transition temperature [108]. This is reached on account of crosslinking formation done by oxidation and condensation during the step [109]. PAN-based fiber thermostabilizes in a range of 200 °C–300 °C and it takes from 30–120 min, corresponding to almost 15% of the manufacturing cost [110–112]. That implies that, using conventional procedures (heating treatment in furnace), thermostabilization requires about 80% of the processing time [113]. This process is preferably conducted in air, that is the cheapest oxidizer gas [114]. From this moment, it is interesting to impose tension to the fiber in order to limit the structure relaxation during heating, and thus, to maintain alignment and orientation of the polymer chain [105]. New techniques have been studied in order to minimize costs and time, where processes such as plasma, electro-beam-assisted cyclization and microwave can be highlighted [65, 113].

Carbonization and graphitization are very similar methods differing in orientation and crystallization degrees, according to the temperature imposed. Structurally, in the carbonization process, graphene sheets (carbon atom layers) are stacked irregularly or randomly folded, tilted or split; in the graphitization process, graphene sheets are stacked parallel in a regular manner [94]. These steps are carried out in an inert atmosphere, removing all non-organic elements from the fiber. These elements are volatilized as CH₄, H₂, HCN, H₂O, CO, CO₂, NH₃, and others, enriching carbon-carbon bounds [4, 109, 115]. In other words, precursors with high amounts of heteroatoms have greater mass loss in the carbonization step because of its gasification, generating a fiber with pores and micropores that compromise its mechanical properties [4, 109, 115–117]. Carbonization step enriches carbon percentage while graphitization converts its molecular structure into a different configuration (see figure 5) [4]. For PAN-based, this step corresponds to about 23% of the manufacturing process cost [112].

Surface treatment is usually done in order to provide a better interaction between the fiber and polymeric-matrix as a guarantee of quality for composites. It oxidizes the fiber surface, creates some roughness and includes functional groups. Oxidation procedure can be conducted by liquid (such as sodium hypochlorite or nitric acid)



or by using gases such as air, ozone or carbon dioxide [118]. An electrolytic coating is also a possible oxidative procedure [93, 118]. Many companies kept these procedures confidential [93].

Sizing is a subsequent step after surface treatment, where a thin resin layer is placed on the surface of the fibers. This procedure has the intention of protecting the physical characteristics of the fiber, while lubricating it, besides making it easy to handle when they are still brittle at this point [93, 118]. ‘Coating’ must be compatible with the matrix resin. Parameters at this point are critical in the carbon fiber specification [93, 115].

There is a subtle difference between carbon fiber, carbon nanofiber and carbon nanotube. To defer fiber and tube, the length/diameter ratio should be evaluated. Carbon fiber is defined as a one-dimensional filament with a ratio of length to radius greater than 100, while tube has lower values [30]. Carbon nanofiber has its diameter in nanoscale, generally around $0.1 \mu\text{m}$ [30]. In terms of production, carbon nanotube is supplied in powder form; carbon nanofiber in the form of ‘carpet’ with randomly dispersed fibers, resembling a web; and carbon fiber in the form of multifilaments to be woven by industries [30].

These multifilaments composing of what is called a tow of fibers are generally expressed with a nomenclature such as 12 K. This ‘K’ after a number indicates 1,000 times. So, a 12 K fiber has 12,000 filaments. The 1 K, 3 K, 6 K, 12 K and 24 K tow are considered small tow; products higher than 24 K are considered wide tow, while 48 K and 50 K are mostly used [119].

In 2016, Japan, Mexico and the United States of America together were responsible for 63% of the global carbon fiber production capacity. Among the ten biggest carbon fiber manufacturers around the world, it is noteworthy that Toray Industries, Inc. was responsible for 31.2% of global marketing in 2016. This was favored because the company acquired ZoltekTM in 2014, incorporating its production. In terms of applications, aerospace is responsible for 30% of the global demand, followed by the automotive sector (22%), wind turbines (13%), sport and leisure (12%) and construction (5%) and others (18%) [5–7].

With an increasing demand for carbon fiber around the world, many producers are investing in capacity expansion and improvements: SGL and BMW doubled their annual production in 2015, and expanded their plants, dealing a joint venture; Mitsubishi Rayon also planned to double its capacity; Ford and DowAKSA agreed to a cooperation by joint research and development; and Hexcel invested in a new factory for carbon fiber production, besides currently building up a new precursor [6, 7].

4. Lignin as a carbon fiber precursor

Carbon fiber capacity production has grown greatly in the world, nevertheless its price has not reduced significantly. Justification can be attributed to the high price of the PAN when it is still responsible for 90%–96% of world’s total production [119–121]. Lignin, as a precursor for carbon fiber production, could reduce its cost by 35% or higher, besides utilizing a renewable by-product material, available in large scale [115].

Lignin-based carbon fiber has been shown to be promising and interesting that several research centers, universities and government agencies have been developing research in the area. Many advantages can be cited when extruding lignin rather than PAN: (a) precursor is independent of fossil source; (b) increased productivity; (c) less energy expenditure in MJ per fiber kg; (d) minimal environment toxicity compared to other precursors; (e) reduced CO_2 per fiber kg compared to PAN; (f) high carbon yield (up to 60%); and so on [30, 101]. A disadvantage is that, by now, lignin-based carbon fiber cannot reach the mechanical properties of high modulus achieved by PAN-based carbon fiber, applied to aerospace. Nevertheless, this disadvantage is overcome by employing the lignin-based carbon fiber in automotive sector and by replacing fiberglass in composites, for example.

Indeed, the automotive segment is the best market integration currently, as it requires low modulus materials (172 GPa) and low tensile strength (1.72 GPa) in which lignin can supplant [30]. An estimated study shows that if 10% of the Kraft lignin were recovered, it would be possible to generate about 16,000 tons of carbon fiber from it, considering a yield of about 45%–50% provided from the material. This amount could be used to produce around 160,000 cars with 600 kg lower weight per car [122]. This application, besides being economically advantageous for the use of lignin among all studied, is also feasible in order to save 50 times more energy compared to its use for combustion as a fuel substitute in boilers [122].

Vehicles 10% lighter in weight implies a 6%–8% savings in fuel economy, approximately [123]. This option of application is very appropriate and completely matches with future needs for reduction policies for greenhouse gas emission, set for 2020 under Kyoto Protocol. It is known that the weight of the vehicle is a factor that entails gas emission. However, to reach the desired goal, a 50% weight reduction is necessary. By that, carbon fiber reinforced composites can reduce components weight up to 60% with the same automotive functionality [112, 124]. PAN-based carbon fibers are very expensive for that use in which lignin-based has become an interesting candidate.

Some estimates show that, in order for PAN-based fibers to attend to the automotive market segment, prices would reach about 40 US\$/kg. Experts consider 11 US\$/kg an accessible price for its application [30]. With an environmental appeal, and all the advantages mentioned earlier, Switzer developed the first prototype vehicle in the world with a roof made of a lignin-based carbon fiber composite. The car had also been equipped with electrodes in the battery containing lignin-based carbon fiber [125, 126]. The merit comes from the partnership of Innventia, Swerea, Blatraden and KTH Royal Institute of Technology. The fiber used to build the prototype was provided by Innventia, which uses lignin derived from the LignoBoost process [127].

Another sector of applications with potential growth for lignin-based carbon fiber use is wind turbine. Nonstructural applications also should not be discarded. Despite having a smaller market, its use for manufacturing of thermal insulation (civil engineering), battery electrodes (excellent conductivity), and hydrogen gas storage (fiber with high pore volume) is entirely feasible [122].

Historically, the first lignin-based carbon fiber produced was developed in Japan (1964) [128] and the process was patented by Otani *et al* (1969), for Nippon Kayaku Co. [129]. The patent describes a process using alkaline lignin, thiolignin and lignosulphonates, spun by melt, wet and dry extrusions with an emphasis on these last two processes. The company started commercializing the fibers in 1968 for gasket application, developed a pilot plant in 1970, and ceased the production in 1973 because of poor mechanical properties achieved by the fiber [128]. Later, in the same decade, a similar process was patented by Mannsmann *et al* (1973), using an aqueous solution of lignin, with an addition of polymer like polyethylene oxide (PEO) [10].

While lignin-based carbon fiber technology is under full development, the manufacturing area (spinning, oxidation and carbonization/graphitization) has been mostly studied [130]. Surface treatment and sizing still need more information in order to achieve compatibility with the composite material [130].

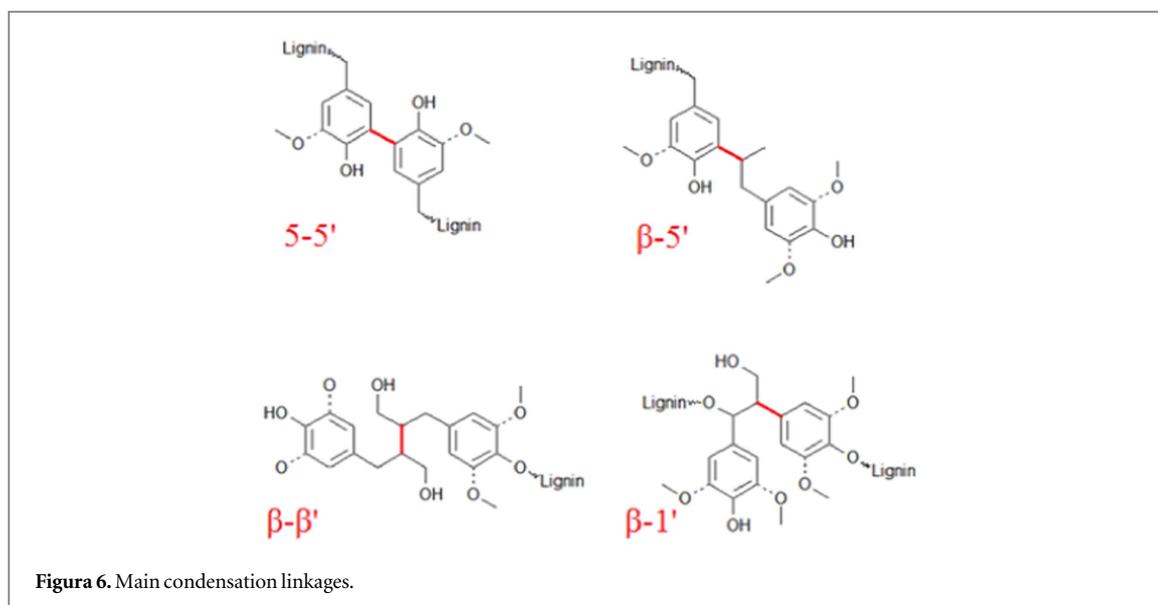
4.1. Lignin extrusion

The ability to use a bio-derived by-product as raw material to manufacture carbon fiber decreases petroleum dependency and, environmental impacts, and improves availability [77]. Moreover, lignin has the versatile disposal to be extruded in different manners, just like polymers. Spinning and extrusion steps are responsible for the tenacity, morphology and diameter of the precursor fibers [131]. For example, while the fiber is being extruded it has a specific diameter; but as spinning starts stretching the fiber, it aligns the molecular chain improving the orientation and decreasing the diameter. This decreases voids and provides tenacity to the fiber.

Melt-spinning is generally the preferred extrusion method, when it does not require any other resource besides the fusion of the raw material [132]. This may be another advantage of the lignin, because it 'can be melted' and does not require toxic solvents as PAN does. It was said that it can be melted, but its fusibility is bound to some parameters that can limit or facilitate the property. Here, these parameters will be divided into structural and operational.

4.1.1. Structural parameters

- (a) Condensation: syringyl lignin melts easier compared to guaiacyl lignin [133]. This thermal behavior is due to the availability of the guaiacyl and p-hydroxyphenyl C₅-position, that easily forms condensed structures. They are more recalcitrant, recalcitrant and disfavor fusibility [134]. These condensed structures are due to the formation of β -5' and 5-5' (Figure 6) linkages, which limits molecular rotation [135]. Softwoods have higher frequency of these linkages [135]. Besides its natural formation, these linkages are more pronounced because of isolation procedures that usually rearrange lignin structure, favoring carbon-carbon and alkyl-aryl ether linkages, as cited before. Another considerable linkage is β - β' , although it is more evident in



syringyl lignin [136]. Furthermore, as temperature increases, some functional groups tend to crosslink impeding molecular rotation, making it difficult to extrude [1].

- (b) Carbonyl: carbonyl concentration favors thermal mobility [136]. It is mainly encountered in technical lignin of herbaceous that has a high concentration of phenolic or cinnamic acids (ferulic and p-coumarilic) [137]. These structures are by-products of an extraction process when protolignin does not have phenolic acids [36]. Their chains are naturally esterified hindering C-C linkage on aliphatic chain (see item c below), that justifies a better plasticity. In contrast, one must have in mind that herbaceous has more guaiacyl and p-hydroxyphenyl structures, which are condensable units that can hamper thermal mobility. This suggests research over compensation effects [136].
- (c) Phenolic and aliphatic hydroxyls: hydroxyls in lignin structure have strong influence in thermal mobility. Aliphatic hydroxyls, mainly those at C_γ-position, decrease thermal mobility [44]. This is due to their preference to form intermolecular hydrogen bonds, which play a dominant role in the infusibility of the lignin [44, 136]. Nevertheless phenolic hydroxyls are more likely to form intramolecular hydrogen bonds, mainly with methoxy groups. Intramolecular hydrogen bonds between phenolic hydroxyl groups hinders aliphatic intermolecular hydrogen bonds, favoring thermal mobility [138]. A higher concentration of phenolic hydroxyl group is desired for melt extrusion process; while aliphatic hydroxyl groups should be avoided or eliminated.
- (d) Aryl-ether bonds (β -O-4'): evidence has shown that a higher ratio of aryl-ether linkages, β -O-4' specifically, increased thermal mobility [136]. A hypothesis to justify the factor may be attributed to its possible linear formation [44, 136]. It is worth mentioning that despite β -5' and β - β' linkages have also suggested linearity on the structures, they are formed by C-C linkages (condensation bonding), while β -O-4' linkage is a ether linkage.
- (e) Decomposition temperature (T_d): low T_d is harmful to melt extrusion. The lower its value, the greater volatiles generated and consequently, there is a compromise in a continuous extrusion, besides leading voids and defects to the fiber [136]. Presence of phenolic acids, impurities (like carbohydrate and proteins) and aliphatic hydroxyls contribute to decrease T_d , which may explain why their content must be reduced [136].
- (f) Glass transition temperature (T_g): T_g is related to thermal mobility and therefore a low value favors its fusibility. Its property is intrinsically related to the parameters mentioned earlier. For example, aliphatic hydroxyl groups collaborate to form intermolecular bonds, which reduce thermal mobility and then, consequently, increase T_g . Carbohydrates, proteins and every impurity can influence T_g [57, 136]. Condensation reactions decrease free volume, increasing T_g [136].

4.1.2. Operational parameters

According to the Oak Ridge National Laboratory (ORNL)—US government agency—, lignin needs some preliminary requirements to reach the ideal condition to be used as a precursor to melt-spin. The settings to be

achieved were: purity degree higher than 99%; volatile content less than 5% at 250 °C; ash content less than 1000 ppm; less than 500 ppm of particulate matter with a diameter higher than 1 μm ; and carbohydrate residual lower than 500 ppm [101, 139, 140]. These criteria were determined experimentally/empirically and provide a fusible lignin ready to be extruded [140]. That is why they were considered operational parameters.

Despite lack of specification highlighting the considered contaminants to be expressed in a maximum of 1%, according to Baker, Griffith and Compere (2005), lignin-based carbon fiber requires methods to extract salts, particulate matter and volatile [141]. Moreover, carbohydrates must be minimized because of its compatibility with water. Hosseinaei *et al* (2017) also mentions protein-based amounts as impurities that should be avoided [142]. These components are the same limited by ORNL that suggests that the sum of all of them might not reach 1% at all.

Impurities limit extrusion, besides compromising fiber properties. Contaminants, which may impair the quality of the fiber, are grains of sand, diatom, cellulosic fibers, water, inorganic, carbohydrates, proteins and volatiles [77, 117].

- (a) Carbohydrates: lignin forms a complex with polysaccharide (cellulose and hemicellulose) by strong linkages, hard to dissociate [73]. They are known as lignin-carbohydrate complexes (LCC) and removal methods are required when these polysaccharides contribute to plug spinneret holes [77]. Further, they increase water bounding with lignin and have low carbon yield [143]. Hemicellulose is the major carbohydrate presented, because its strong interconnected covalent bound [4, 71, 74]. *In natura*, hemicellulose association reaches values higher than 50%, while in technical lignin the percentage ranges from 2% to 8% wt. [70, 73, 75]. According to Zhou *et al* (2010), there is little evidence of lignin association with cellulose [72], although molecular dynamics calculations have proven their interaction [144]. Reduction on carbohydrate amounts can be reached with a selective technique such as membranes [145, 146] or using polysaccharide enzymes [70, 147].
- (b) Proteins: carbohydrates may either be responsible for traces of recalcitrant proteins identified with the lignin, because of the possible bound between them [76]. Moreover, there is some evidence of covalent linkages between lignin and proteins; or condensation between lignin and protein-derived materials; or even possible coprecipitation and/or physical trapping of protein-derived materials with lignin [136, 148]. Hot aqueous acid usually easily removes these amino acids [58, 149].
- (c) Particulates: particulate matter encountered are comprised of sand (silicates), diatom and cellulosic fibers and, besides being infusible, they can clog the holes of the extruder and may cause structural defects to the fiber manufacturing [77]. Particulate matter can be removed by filtration with a specific porosity filter media.
- (d) Ashes: ashes are related with inorganic materials. They are present because of the extraction procedure or silicates from remaining particulates. They can be removed by extensive washing with hot aqueous acid [58].
- (e) Water: water associates with the hydrogen of the phenolic and aliphatic hydroxyl groups of the lignin, making hydrogen bounds. It acts as a strong reducing agent, and must be eliminated once chars lignin invalidates its fusibility [139]. Moreover, water can act as a volatile, promoting voids during melt-spinning [143].
- (f) Volatiles: volatiles can be moisture, or other solvent used during isolation, recovery or purification procedure. Water and volatiles can be removed by vacuum treatment at elevated temperatures [4, 139]. This procedure must be applied after the washing procedure for ash removal.
- (g) Polydispersity: its high value provides an increase in softening temperature [128]. Many authors have reported that a low polydispersity, that is, a better homogeneity of the lignin, favors the extrusion [115, 150]. Nevertheless, it was observed that lignin fractions of low molecular weight cannot be spun into fibers because it cannot reach an adequate viscosity; albeit short chains may act as plasticizer agents [65]. High molecular weight fractions cannot melt, hardening the lignin; but it provides a sufficient valor of viscosity [65, 151]. Thus, a certain polydispersity index is desired to favor melt-spinning [65]. This parameter must be considered once an increase in the polydispersity implies an increase in the melt temperature. These antagonistic conditions need to be carefully studied.

There is no criteria limiting, or even highlighting, sulfur as an undesirable contaminant, although its participation affects the quality of the final product. Lignosulfonates, for example, have high amounts of sulfonic groups at α -carbon position (see figure 3) which is highly reactive and can cause thermal instability at low

temperatures ($<200\text{ }^{\circ}\text{C}$) [152]. At high temperatures ($>600\text{ }^{\circ}\text{C}$), sulfur can act as an inhibitor of the degradation [152]. Moreover, as a heteroatom, during carbonization step, its presence will favor the formation of porous, providing a fiber with structure commitments (voids and defects). Sulfur can be presented as sulfate ion, elemental sulfur, adsorbed polysulfide and organically bounded [153]. Sulfur (organically bounded) removal is a challenge, in which catalytic processes using Raney-Ni have been tried. Nevertheless, the best removal percentage reached, with softwoods, was 49% [153]. According to Vishtal and Kraslawski (2011), besides being unfeasible to be implemented industrially, it is costly [58, 153, 154].

4.1.3. Other extrusion processes

As mentioned before, melt-spinning is the most studied method to extrude the lignin. It is possible to find some research using wet and dry spinning as well [32, 152]. It is worth mentioning that both of these procedures require soluble lignins, which depends on the type of the lignin and extraction procedure. Another method that can be mentioned with significant results is the melt-blown process [112, 140]. The difference is that melt-blown process manufactures a mat with pieces of fibers (resembling a web), while others manufacture a continuous fiber. Electrospinning is also a considerable alternative to the melt spinning, although it also requires soluble lignin and it is suitable to provide carbon nanofiber instead of carbon fiber [30]. There may be cited, though less common, centrifugal spinning and short barrel extrusion, large-scale spinning technology and low residence time (melt-blown is included), and phase inversion extrusion, that uses low heat (like electrospinning) [8].

Although electrospinning is considered a neophyte technique in industrial terms, it has been studied carefully. Melt-blown, in contrast, has been considered a more robust technique, with interesting results for lignin use.

The as-spun fibers obtained in this step can be called lignin green fiber or only lignin fiber.

4.2. Oxidation

Even called thermostabilization, the oxidation process is a subsequent step after obtaining the lignin green fiber. This step consists of an increase of T_g in order to avoid softening the fiber before the carbonization step. This is due to the fact that T_g is far below the desired temperature to carbonize. To increase T_g , during this step, oxidized groups are introduced and crosslinking are formed [108]. So, this step is responsible to remove the thermoplastic behavior from the lignin. By that, oxidation at slow heating rate can increase T_g faster than the temperature of the system (oven or muffle). High heating rates melt the fiber, making the process impossible [108]. Optimization procedures are always required.

The oxidation process is generally conducted in air, as it is a simple method and has a low cost [106]. Modification in its structure is not well characterized, although it is known that at low temperatures, oxidation reactions comprising for demethoxylation, degradation/conversion of lignin interunit linkages or aliphatic side-chain functionality, and formation of carbonyl and carboxyl groups [108, 109, 155]. Once formed, as temperature increases crosslinking is formed because these groups are inserted into ester and anhydride linkages [108, 155]. Besides, rearrangements in the lignin structure occur favoring condensation linkages that comprises for recrudescence.

Generally, thermostabilization temperature ranges between $200\text{ }^{\circ}\text{C}$ – $300\text{ }^{\circ}\text{C}$ and heating rate must be analyzed for each case, taking into account the operational feasibility [156]. This rate evaluation is an important factor to be controlled, even because during thermostabilization, exothermic reactions occur [157, 158]. By this step, a tension should be employed.

In a statement, it was observed that thermostabilization highly influences the performance of the end carbon fiber. Tests have shown that for greater yield of final product, green fiber must be stabilized in a optimum range of $260\text{ }^{\circ}\text{C}$ – $290\text{ }^{\circ}\text{C}$ [159]. Over this temperature range, aromatic rings condensation and condensation reaction of carboxylic acid are much more evident. Competitions between formation of aromatic structure and pyrolysis are assigned at this temperature range. If the temperature is above $290\text{ }^{\circ}\text{C}$, the disorder of the turbostratic structure may be highlighted once pyrolysis disrupts ordered aromatic structures, comprising the carbonization step; if it is below $260\text{ }^{\circ}\text{C}$, structure changes only start forming turbostratic structure [156, 159].

As it was said before, technical lignins from softwood have more crosslinked structures that hinders its fusion. During the thermostabilization step, this fact can be considered an advantage once it makes lignin more susceptible to the oxidation than hardwoods. Moreover, softwoods are considered more branched and have higher amounts of oxygen (favors autocatalytic stabilization) [156]. These reasons may justify why softwoods are difficult to melt, but easier to thermostabilize compared to hardwoods [156].

Procedures to thermostabilize lignin fibers are the same used for PAN-based and pitch-based carbon fibers. Thereby, no special equipment is required. However, conventional procedures in this step are responsible for around 80% of the whole conversion line production of the carbon fiber [113]. This is due to the low heating rate required for an effective fiber oxidation. Therefore, plasma has been tried in order to optimize and increase the

conversion line, without making the process expensive [94, 113]. Some other processes have been equally tried with significant advances: electron beam irradiation, ultraviolet light and thermochemical process [94, 113, 158].

Whilst low heating rate is required, lignin-based carbon fibers require less time and lower temperature to stabilize compared to PAN-based fibers [160]. The capability to stabilize faster than conventional procedures is because oxygen diffusion is easier in lignin than in PAN, which is dense and hard to allow oxygen penetration into the inner part [30].

4.3. Carbonization and graphitization

After being thermostabilized, fibers must be carbonized to provide mechanical, electrical and thermal properties inherent in the carbon fiber. Carbonization and graphitization are conducted under an inert atmosphere, and the temperature range is not unanimous among the authors. Some consider that carbonization is conducted up to 1000 °C, while graphitization is submitted up to 3000 °C [94, 161]; others assign that carbonization step is ranged between 1000 °C–2000 °C, while graphitization is between 2000 °C–3000 °C [115]; there are some others that say graphitization is reached after 2500 °C [162]. All these differences are on account of the precursor used. Depending on the raw material, carbonization and graphitization occur in different sets of temperature. As a matter of fact, one takes the optimized procedure for some precursor and applies it as a rule for every other. For lignin use, carbonization is in a range of 500 °C–1000 °C, while graphitization is reached in temperatures up to 1200 °C [32, 163]. An evaluation using lignin-based fibers from Lignoboost[®] procedure showed that their tensile strength increased at temperatures above 600 °C [164]. Besides, heating rate interval from 1 to 40 °C · min⁻¹ did not show any effect on strength manufacturing [164]. Graphitized fibers may optionally be called graphite fiber.

During the step, greater heating rates are employed compared to thermostabilization. Once it consumes high amounts of energy, this step is also costly. Although faster, carbonization rate should not be too fast in order to avoid defects to fiber structure [94]. Slow rates are not desirable either as it causes too many losses in inert air used [94]. Similarly as in thermostabilization, new techniques have been tried to minimize costs and to accelerate the process. Microwave assisted plasma technology has been shown as a suitable procedure to replace conventional steps, where previous research presented faster processing (in orders of magnitude), reduced operational cost (reduction around 21% for PAN-based fibers), lower temperature operation, reduced unit capital investment, and so on [113, 124].

During thermostabilization and carbonization steps, losses in mass are significant. These losses are associated with volatiles formed during thermostabilization high temperatures, and in the carbonization initial stages, because of dehydration and decarboxylation reactions of those steps [156]. Condensation reactions are also present.

Tension is fundamental during this phase when microscale porosity is introduced [109], and an alignment of the structure is desired. At the beginning of carbonization, the remaining methoxyl content is reduced, carbonyl and carboxyl contents decrease and the proportion of aryl and condensed aryl carbons increases [155]. When temperatures reach up to 900 °C, all functional groups are eliminated, remaining the carbon backbone in a disordered turbostratic degree [165]. By using conventional procedures of thermostabilization and carbonization, the total yield obtained can reach around 30%–50% [4, 9, 112, 166].

The correct knowledge of the thermal behavior of the lignin is an important step because of the relationship among thermostabilization rate, thermal degradation, crosslinking and mechanical properties [32]. Some studies carbonized the fiber directly, without thermostabilizing it. Many of those must be carefully analyzed when possible, owing to the high temperature required to melt spin, which was high enough to degrade the lignin [134]. For those, generally, the end-product showed poor mechanical properties. One might be careful in order to avoid degradation temperature during melt spinning with the penalty of compromising the product. This might be possible, for example in Soda lignins, where soft temperature is higher than the degradation temperature [152].

4.4. Lignin-based carbon fiber

A summary table with the most important data of this subsection is provided on table 3.

4.4.1. Neat lignin

When studies about lignin-based carbon fiber started, manufacturing knowledge was limited. The process of extrusion itself was a hurdle to overcome. As cited before, melt spinning was always the desired focus, as it would avoid any cost with solvents or coagulation baths in the process. There was a big challenge because when neat lignin could be spun as fiber, it generally provided a disrupted/fragmented process or a brittle fiber [4, 167, 168]. Because of this discontinued processing and/or apparent limitation to melt, the first commercial lignin-based carbon fiber was obtained blending it with some polymers (see section 4.4.2.1). However, the purpose for

Table 3. Summary of lignin-based carbon fiber attempts.

	Type	Extraction procedure	Melt spinning temperature	Thermostabilization Temperature/Heating rate	Carbonization temperature/Heating rate	Results	Comments	Source
Neat lignin	Hardwood	Organosolv (acetic acid)	210 °C	250 °C/0.5 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	No properties provided;	Softwood lignin was prior purified to melt spinning	[151]
	Softwood		350 °C–370 °C			Fibers with low performance		
	Hardwood	Kraft	195 °C–228 °C	250 °C/2 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Fiber obtained	Devolatilization under vacuum, at 145 °C favored extrusion;	[9]
	—	Organosolv	138 °C–165 °C	250 °C/0.2 °C · min ⁻¹	—	—	Content of hydroxyls reduction improved extrusion	—
	Harwood	Kraft	—	250 °C/0.05 °C · min ⁻¹	1000 °C/2 °C · min ⁻¹	Fiber with poor mechanical properties	Preheat of 48h, at 80 °C, under vacuum prior to extrusion;	[169]
Lignin-polymer	Hardwood	Kraft	150 °C–228 °C	250 °C/0.2–3 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Fibers obtained suitable for general performance	Lignin blended with PEO (less than 5% w/w)	[9]
	Softwood	Kraft	—	—	—	—	No fiber obtained even with an addition of 25 % of PEO;	—
	Hardwood	Kraft	130 °C–240 °C	250 °C/0.2–2 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Fibers properties better than pitch-based ones	Preheat of 30 min, at 160 °C, under vacuum;	[177]
	Hardwood	Kraft	Wet spinning	—	—	Up to 800 °C	Lignin blended with different ratios of PET and PP; Lignin-PET provided better properties	[179]
	Hardwood	Kraft	Wet spinning	—	—	Fiber obtained	Lignin was prior purified (acidic aqueous solution); Lignin was copolymerized with PAN;	[179]

Table 3. (Continued.)

Type	Extraction procedure	Melt spinning temperature	Thermostabilization Temperature/Heating rate	Carbonization temperature/Heating rate	Results	Comments	Source	
Lignin-polymer	Softwood	Kraft	180 °C	1st step: 105 °C/1 °C · min ⁻¹ 2nd step: 250 °C/0.25 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Fiber with excellent morphology	Wet spinning with a coagulation bath of hot water (60 °C–90 °C) Lignin was prior esterified	[180]
	Hardwood	Kraft	220 °C–240 °C	280 °C/0.25 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Fibers obtained	Derivatized lignin was blended with PLA; Best fiber property was 75/25 w/w (Lig/PLA) Lignin was prior purified and fractionated; Lignin was blended with PLA; Best property was 80/20 w/w (Lig/PLA)	[181]
	—	Kraft	Electrospinning	250 °C/1 °C · min ⁻¹	1000 °C/5 °C · min ⁻¹	Fibers obtained	Lignin was prior fractionated; Fractionated lignin was blended with PAN;	[46]
Mixture of lignins	Hardwood	LignoBoost	140 °C–220 °C	250 °C	1st step: 600 °C/1 °C · min ⁻¹	Good quality of fibers	Lignin fractionated (ceramic membrane)	[168]
	Softwood	LignoBoost		0.2 °C · min ⁻¹	2nd step: 1000 °C/3 °C · min ⁻¹		Lignin fractionated (ceramic membrane)	
	Softwood	LignoBoost				Lignin with no fractionation; Lignin blended with hardwood fractionated lignin; Ratio of softwood and fractionated hardwood lignin ranging 93%–97% w/w		
	Hardwood	Organosolv	180 °C–185 °C	250 °C/0.05–0.5 °C · min ⁻¹	1st step: 600 °C/3 °C · min ⁻¹ 2nd step: 1000 °C/5 °C · min ⁻¹	Fibers obtained; Lower amount of switchgrass	Hardwood organosolv lignin blended with soda switchgrass lignin; 15%-50% (wt.) of soda lignin were add	[142]

Table 3. (Continued.)

Type	Extraction procedure	Melt spinning temperature	Thermostabilization Temperature/Heating rate	Carbonization temperature/Heating rate	Results	Comments	Source	
Blend with other material	Hardwood	Kraft	260 °C–280 °C	200–280/	1st step: 800 °C	Shell-core fibers; lignin favors mechanical properties	Lignin blended with pyrolyzed fuel oil (PFO);	[189]
				1 °C · min ⁻¹	2nd step: 2800 °C			
Lignin-fillers	Softwood	Kraft	130 °C	—	Run A: ramp of 90 °C–800 °C/5 °C · min ⁻¹	Fibers with poor mechanical properties	Lignin filled with 28% of n-methyl pyrrolidione;	[128]
	—	Pyrolytic Lignin	105 °C–180 °C	250 °C/0.5 °C · min ⁻¹	Run B: ramp of 90 °C–250 °C/10 °C · min ⁻¹ followed by ramp of 250–1000 °C · min ⁻¹ /5 °C · min ⁻¹			
Derivatization	Hardwood	Steam-exploded	155 °C–180 °C	210 °C	1000 °C/5 °C · min ⁻¹	Fibers with good tensile strength and low modulus	Lignin derivatized by hydrogenolysis	[1]
	Hardwood	Steam-exploded	280 °C	1–2 °C · min ⁻¹ Ramp of 60–300 °C/1 °C · min ⁻¹	1000 °C/1 °C · min ⁻¹			
	Hardwood	—	220 °C	—	—	Yield greater than 40%	Lignin derivatized by phenolization with catalytic (acetic acid)	
	Softwood	—	220 °C	240 °C/0.2 °C · min ⁻¹	1150 °C/4 °C · min ⁻¹	Fibers obtained;		[197]

Table 3. (Continued.)

Type	Extraction procedure	Melt spinning temperature	Thermostabilization Temperature/Heating rate	Carbonization temperature/Heating rate	Results	Comments	Source
Softwood	Solvolysis	145 °C–172 °C	250 °C/0.5 °C · min ⁻¹	1000 °C/3 °C · min ⁻¹	Study provided a patent Fibers with cracks over axial surface and porous over radial surface	Lignin derivatized by acetylation (acetic anhydride, acetic acid or acetyl chloride); Acetylation can be provided with or without catalytic (pyridine); Lignin derivatized by PEG with sulfuric acid;	[135]
Hardwood	Organosolv	153 °C–158 °C	250 °C/5 °C · min ⁻¹	800 °C/5 °C · min ⁻¹	Fibers with properties to be used as adsorbent and anode	Prior to thermostabilize, fibers were immersed in aqueous solution of HCl Lignin derivatized by esterification (phthalic, succinic, acetic and maleic anhydrides) using THF as solvent.	[109]
Softwood	Kraft	145 °C	220 °C/0.1–0.25 °C · min ⁻¹	1000 °C/4.5 °C · min ⁻¹	Fiber with excellent tensile strength	Lignin derivatized by acetylation;	[198]
Grass	Soda	150 °C–170 °C	230 °C/1 °C · min ⁻¹	1000 °C/ 10 °C · min ⁻¹	Irregular fibers with poor mechanical properties	Dry-spinning using acetone as solvent Lignin from sugarcane bagasse; Lignin derivatized by esterification (octanoyl and lauroyl chlorides)	[199]

manufacturing the product using neat lignin has encouraged parallel and continuous studies. It provided more knowledge about the manufacturing process and how to melt the macromolecule. Many attempts were made to use neat lignin.

Kubo, Uraki and Sano (1998) used hardwood (HAL) and softwood (SAL) lignins extracted by atmospheric acetic acid pulping. HAL could provide melt spinning at 210 °C. SAL was infusible and this was assumed to be due to content of 'infusible fraction'. One can conclude that these infusible fractions were chains with high molecular weight. After fractionation with acetic acid, 70% of infusible fractions of SAL were removed (SAL-L). SAL-L could be melt spun at 350 °C–370 °C, and because of this high temperature used, thermostabilization could be dismissed. Nevertheless, a fraction of SAL-L fibers, jointly with HAL fibers, was thermostabilized at 250 °C (heating rate, 0.5 °C · min⁻¹). All fibers were carbonized at 1000 °C (heating rate, 3 °C · min⁻¹). There was no significant difference between thermostabilized SAL-L fiber and the directly carbonized one, in terms of mechanical properties. The fibers obtained were considered able to be employed as activated carbon fiber because of the porosity along their structure [151]. Despite its low performance, important knowledge could be obtained: the molecular weight distribution is one of the parameters that drives the process.

Kadla *et al* (2002) performed a preheat treatment at 145 °C, for 1 h, under vacuum to improve organosolv and hardwood thiolignin (HWKL). Organosolv lignin could be spun at 138 °C–165 °C, while HWKL lignin at 195 °C–228 °C. Thermostabilization was performed at 250 °C, held for 1 h, where organosolv used a heating rate up to 0.2 °C · min⁻¹ and HWKL, 2 °C · min⁻¹. Carbonization was conducted at 1000 °C using a heating rate of 3 °C · min⁻¹. According to the authors, pretreatment favored the extrusion because of devolatilization of impurities and the reduction of hydroxyl content [9].

Baker, Gallego and Baker (2012) separated hardwood thiolignin into two parts: as received (HWL) and purified by organic solvents (HWL-OP). Both HWL and HWL-OP were preheated at 80 °C under vacuum for 48 h. Preliminary studies showed that HWL had 2.7 wt% of ash at 1000 °C, while HWL-OP was undetectable. HWL-OP was also characterized with a low molecular weight fraction. HWL exhibited very poor spinnability, being considered impractical for melt spinning. HWL-OP could melt spin easily for hours. A thermostabilization study was carried out where the HWL-OP fiber could be stabilized at 250 °C under heating rates less than 0.05 °C · min⁻¹. Carbonization used heat treatment to 1000 °C at a heating rate of 2 °C · min⁻¹. Poor mechanical properties were obtained, even though purification and thermal treatments were applied. The authors concluded that contamination (mineral and carbohydrates) is harmful to the extrusion, and low molecular weight acts as plasticizers agents [169].

Many other attempts were tried [101, 115, 135, 168, 170–172]. Each one added new insights to lignin melt spinning: (a) low molecular weight chains act as plasticizer for melt spinning while higher molecular weight chains provide desired viscosity and T_g [173]; (b) neat lignin from conventional extraction, without any purification procedure, provides brittle fibers; (c) devolatilization procedure before melt spinning favors extrusion. It was due to this research that Baker and co-workers could obtain the correct specifications now known (see section 4.1.2) for lignin use as a carbon fiber precursor [141, 174].

4.4.2. Lignin blend for extrusion

4.4.2.1. Lignin-polymer

Polymers can be incorporated to lignin using melt, wet or dry spinning. When melt extrusions are prioritized, the approach takes advantage of some thermoplastic polymers that interact with lignin and work as a vehicle to extrude the blend and form the fiber. The polymer acts favoring the fusibility and fluidity to the extrusion and gives some flexibility to the material. Sometimes, for a better interaction between lignin and polymer, some derivatization on its structure is necessary. This chemical modification is focused on decreasing the high polarity of hydroxyl groups to favor lignin-polymer linkages. The polymer/lignin melts and extrudes to form the green fiber blend. As subsequent thermal treatments happen, the polymer degrades concentrating the lignin to form the carbon fiber. That is, polymer only acts as a vehicle to favor extrusion and to model fiber shape.

In the first patent registered on lignin-based carbon fiber, different types of lignin (alkali-lignin, lignosulphonates and thiolignin) were dissolved in a solvent with polyacrylonitrile, polyvinyl alcohol (PVA) or viscose to, preferably, dry spinning. It might have highlighted the use of lignosulphonates with polyvinyl alcohol, where the process was marketed producing the so called Kayocarbon fiber, manufactured by Nippon Kayaku Co. from 1967–1973 [115, 129, 175]. The main advantage of this procedure was the cost efficiency, high carbon yields and absence of the thermostabilization step [65].

Li Mylinár and Sarkanen (1997) rehearsed improvements in melt-flow index and extrusion-molded with a blend of lignin (85% weight), poly(vinyl acetate) and plasticizers. They were not interested in obtaining carbon fiber, but the blend could provide high tensile strength and moduli. The results are noteworthy, and they concluded that mechanical properties of lignin-based materials are dependent on the interaction between polymer and intrinsic properties of lignin [176].

Kadla *et al* (2002) were pioneers on polymer blend use for lignin-based carbon fiber. Poly(ethylene oxide) (PEO) was used with commercial available lignin (thiolignin) provided from hardwood (HWKL) and softwood (SWKL). For HWKL, carbon fibers could be obtained when less than 5% (PEO/lignin w/w) was used. Carbon fiber overall yield achieved was 45%. SWKL could not melt to provide fibers, even into a range of 25% of PEO [9]. Studies suggested an amount of over 37.5% to favor the extrusion [177]. Although HWKL could be spun without any polymer addition, processability and brittleness were improved with the blend. The good spinnability and the other improvements were reached due to intermolecular hydrogen bond between lignin and PEO and the magnitude of the noncovalent attractive interactions between the individual molecular Kraft lignin [177]. A similar conclusion could be obtained later blending lignin with PVA by melt extrusion [178].

Kubo and Kadla (2005) blended hardwood thiolignin with polyethylene terephthalate (PET) and poly(propylene) (PP). Specifically, PP was tested with different molecular weights and types (isotactic and syndiotactic). Both polymer blends (PET and PP) could provide good fiber spinning, with the particularity that only PP with medium molecular weight was able to be continuously spun into fiber. It could be noted that lignin-PET blends were miscible while lignin-PP provided heterogeneous fibers. The homofibers obtained were thermostabilized carefully with heating rates up to $2\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$, in order not to fuse together. For the samples tested, lignin-PET blend (75/25 w/w) provided the best mechanical properties. Comparatively, this best fiber has a tensile strength and a modulus 1.6 and 1.5 times, respectively, higher than the best fiber obtained by lignin-PP. Moreover, it provided better properties compared to isotropic pitch-based fiber [167].

According to Marandur *et al* (2012), lignin was copolymerized with PAN with specific conditions. PAN-lignin copolymer (16% wt in DMSO solution) was wet spun by a spinneret with 150 holes, each diameter with $50\text{ }\mu\text{m}$, in a coagulation bath containing hot water ($60\text{ }^{\circ}\text{C}$ – $90\text{ }^{\circ}\text{C}$). Fibers were stretched over the processing. After thermostabilization and carbonization (up to $800\text{ }^{\circ}\text{C}$), fibers presented an overall yield of 56%. The authors did not compare the mechanical properties obtained by this blend to the fibers obtained individually with each raw material, but they conclude that, although improvements and optimization were underway, the method could be efficient for cost reduction carbon fiber production [179].

Chen (2012) used commercial Kraft lignin (softwood) esterified with butyric anhydride. Upon the completion of derivatization, the product (B-lig) was blended with different proportions of polylactide (PLA). Esterification was conducted to a better interaction with the polymer. Lignin-PLA blends were extruded at $180\text{ }^{\circ}\text{C}$; thermostabilization was divided in two steps of heating rates, and carbonization reached $1000\text{ }^{\circ}\text{C}$ in a heating rate of $3\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$. The fibers presented excellent morphology, with the best set of properties into the ratio of 75/25 w/w (B-lig/PLA) [180].

Wang *et al* (2015) purified and fractionated (using a ceramic membrane) a commercial hardwood thiolignin and blended it with different ratios of PLA. Extrusion was conducted in a temperature range of $220\text{ }^{\circ}\text{C}$ – $240\text{ }^{\circ}\text{C}$; thermostabilization reached $280\text{ }^{\circ}\text{C}$ using a heating rate of $0.25\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$, and carbonization was conducted up to $1000\text{ }^{\circ}\text{C}$ at a rate of $3\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$. All the mixtures could be spun into fiber, including lignin with no PLA. The authors observed that PLA addition decreases the tensile strength, but increases modulus. They also noted that lignin-PLA blend (80/20 wt.), which is the greatest concentration of PLA studied, increased porosity. This justifies the decrease of the tensile strength [181].

Li *et al* (2017) fractionated Kraft lignin into water-soluble and water insoluble fractions using a common laccase-mediator system. They tested polymerizing this lignin with PAN. It was observed that after the treatment with the laccase-mediator, both lignin (soluble and insoluble) decreased their OH group (phenolic and aliphatic) content compared to the untreated one. Moreover, the treatment also presented different fractions of molecular weight between soluble and insoluble lignin, with lower values of polydispersity compared to the untreated material. Furthermore, β -O-4', β - β' , β -5' and dibenzodioxocin (5-5/ β -O-4'/ α -O-4') linkages differed in each fraction. Interesting conclusions were observed: decreased content of hydroxyl groups improved a better interaction among lignin, PAN and non-polar solvent; different molecular weights improved alignment of the polymer; linearity of the lignin chain (mainly β -O-4' linkage) improved the interconnection of the polymer. Differing from previous reports, authors mentioned that lower polydispersity helped the improvement of the fiber. Nevertheless, in this case, lignin was used as an additive of the PAN, in which an homogeneous structure provides a better interaction between them. That is different from using neat lignin, which high polydispersity can improve the extrusion [46].

As Li Mylinár and Sarkanen (1997), other authors tried different kinds of blends in order to obtain an extruded material with better properties [176]. Although some of these studies mention the fact of being a preliminary analysis for carbon fiber production, they did not carbonize their obtained blends in order to verify their effectiveness to the proposal. One can consult the literature available to follow the evolution of the research [120, 177, 178, 182–186]. For an effective carbon fiber, using polymers to blend lignin may call attention in their miscibility. If hydrogen bonding or/and acid-base interaction are not adequate, immiscible blends will lead an unsuccessful melt-spinning compromising fiber properties.

4.4.2.2. Mixture of lignin

As hardwoods present better properties to melt and softwoods are better to thermostabilize, some researchers mixed both types of lignin in order to get improvements during manufacturing.

Warren (2008) mentions hardwood/softwood lignin blend as a precursor for carbon fiber. It was reported that hardwood lignin acts as a plasticizer for softwood lignin, but there is not much information about the essays and fibers obtained [187].

Nordström (2013) recovered hardwood and softwood lignins from the black liquor using two different procedures: Lignoboost[®] and the permeate obtained through a ceramic membrane. Neat hardwood Lignoboost[®] lignin (HKL), softwood Lignoboost[®] lignin (SKL), hardwood permeate lignin (HKLP) and softwood permeate lignin (SKLP) were all tested. All samples could spin into fiber, although SKL could not continuously spin and HKL was limited providing a brittle fiber. HKLP and SKLP could easily melt spin. It is noteworthy to mention that it was the first time that a neat softwood lignin could continuously spin. Both SKL and HKL were blended with HKLP, considered as a softening agent, in a proportion range of 1%–95% (wt.), providing a continuous fiber. Carbon fibers with good quality and without visible defects were obtained by neat HKLP, SKLP and SKL with 3 or 10% of HKLP. Authors reported that solid filaments could be obtained, with carbon content ranging from 93% to 97%, and softwood lignin could melt spin into fiber with no synthetic addition or no structural modification [168].

Hosseinaei *et al* (2017) mixed Organosolv hardwood lignin with soda switchgrass lignin in different proportions. They harnessed the knowledge that Organosolv lignins present less amounts of aliphatic hydroxyls and phenolic acids providing a better condition for extrusion, while soda switchgrass lignin has higher amounts of guaiacyl and condensed structures providing a better and faster thermostabilization. The first one would act as a plasticizer agent. Besides this, they tried different heating rates during the thermostabilization (at 250 °C). The authors produced miscible blends (melting the mixture at an extruder in a range temperature of 180 °C–185 °C) and could conclude that a higher concentration in switchgrass lignin results in a higher heating rate during thermostabilization. They also observed that lower amounts of switchgrass lignin with lower heating rate provided carbon fibers with the highest mechanical properties [142].

4.4.2.3. Blend with other materials

In 1992, a report was patented preparing phenylated lignin to be coextruded with amounts of isotropic pitch [188]. Although the procedure was described, no results were presented or cited.

Kim *et al* (2014) blended different ratios of commercial hardwood lignin with pyrolyzed fuel oil (PFO). The blends were dissolved separately in tetrahydrofuran (THF) obtaining an 8% (w/w) solution. THF was considered the most suitable solvent to provide a heterogeneous mixture. PFO acted as a plasticizer. Among the ratios tested, the best was 7:3 (lignin/PFO) and the blend was melt spun at 260 °C–280 °C. A good spinnability was reached and the fiber was thermostabilized from 200 °C to 280 °C at a heating rate of 1 °C · min⁻¹. Carbonization step was conducted in argon in a sequential thermal treatment at 800 °C and 2800 °C. The authors obtained shell-core fibers with good mechanical properties as a promising candidate for the automotive industry [189].

4.4.3. Lignin fillers

Schmidl (1992) used softwood thiolignin with an addition of 28% n-methyl pyrrolidinone (NMP). A continuous fiber could be obtained at 130 °C and no thermostabilization was done. Carbonization was conducted in two different manners under argon atmosphere. Run A used a heating rate of 5 °C · min⁻¹ with a profile temperature of 90 °C to 800 °C (kept for 1 h). Run B had a profile of 90 °C to 250 °C (heating rate, 10 °C · min⁻¹) with 15 min of isotherm, followed by a profile of 250 °C to 1000 °C (heating rate, 5 °C · min⁻¹) with 1 h of isotherm. Both procedures provided fibers, although fibers submitted by run B presented better mechanical properties compared to those submitted by run A. However, the fibers obtained had poor mechanical properties compared to previous lignin-based ones [128].

It is known that biomass pyrolysis process provides three products: syngas, bio-oil and coal. Bio-oil fuel instability is due to pyrolytic lignin, which represents around 20% of the material.

Qin and Kadla (2011) used pyrolytic lignin recovered from bio-oil and filled it with two different organoclays. One of the clays is more hydrophobic (Cloisite 20 A) while the other has an ammonium group bounded with a sebaceous group (Cloisite 30 B). Based on previous work [190], the filler was tested in a proportion of 1%, 2% and 5% by weight of clays. All mixtures could be melt spun. Each sample extruded in a specific temperature, and the fibers were thermostabilized at a heating rate of 0.5 °C · min⁻¹ up to 250 °C. After, carbonization was conducted up to 1000 °C at a heating rate of 3 °C · min⁻¹. It was observed that an increase in clay decreased spinning velocity and increased extrusion temperature. Moreover, increasing up to 1% of clay increased tensile strength, while high concentrations decreased all properties [191].

4.4.4. Derivatization

Besides being thermoplastic, lignin has resistance to flow. During heating, hydrogen bonds are formed, and derivatization can be a good technique to improve thermal and rheological properties, replacing lignin hydroxyls (which are responsible for the formed hydrogen bonds) with functional groups with less polarity [147, 192]. Esterification was employed most, presenting better T_g detection and improvement in molecule plasticity [147, 193].

While esterification has been widely reported in literature, possibly the first register using a modification on lignin by demethoxylation for carbon fiber purpose is described in the patent registered by Gould (1974). Moreover, it is the first melt spinning lignin patent encountered. The author describes the methodology, but does not present examples or results [194].

Sudo and Shimizu (1992) used hardwood lignin obtained by steam-exploded process. They modified it by hydrogenolysis, using Raney-Ni as catalyst and aqueous solution of 2% NaOH under pressure ($50 \text{ kg} \cdot \text{cm}^{-2}$) and temperature ($250 \text{ }^\circ\text{C}$). The modified lignin was preheated and extruded continuously at a temperature range of $155\text{C} - 180 \text{ }^\circ\text{C}$. The obtained fibers were thermostabilized at $210 \text{ }^\circ\text{C}$ using a heating rate of $1 \text{ }^\circ\text{C} - 2 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Carbonization reached $1000 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The procedure provided low yield, good tensile strength and low modulus [1].

The same authors used lignin from two different extraction methods: the same used earlier (EXL-1) and a new one (EXL-2). EXL-2 process used steam-exploded extraction, with aqueous solution of 1% NaOH, pressure of $20 \text{ kgf} \cdot \text{cm}^{-2}$, at $215 \text{ }^\circ\text{C}$. Lignin obtained by EXL-1 was phenolated at $250 \text{ }^\circ\text{C}$ for 3 h and could be extruded and thermostabilized ($300 \text{ }^\circ\text{C}/1 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$). Carbonization procedure was adopted in two manners: using one step directly to $1000 \text{ }^\circ\text{C}$ using the same heating rate; and three ramps of heating, with different rates, up to $1000 \text{ }^\circ\text{C}$. No significant change on mechanical properties was detected by these two heating processes. Lignin from EXL-2 was phenolated using acetic acid as a catalyst. No significant change in lignin property was observed adding the catalyst. This modified lignin was extruded, thermostabilized and carbonized as described before, providing a carbon fiber with similar properties as obtained by EXL-1 process [195]. These techniques were patented by the authors [196].

Eckert and Abdullah (2007) patented a lignin procedure of acetylation, focusing on softwood lignin. The experiments were performed by acetic anhydride, acetic acid or acetyl chloride. When pyridine is used, reaction was conducted up to $50 \text{ }^\circ\text{C}$, while absence of pyridine required a higher temperature ($70 \text{ }^\circ\text{C} - 100 \text{ }^\circ\text{C}$). The acetylated lignin by acetic anhydride and pyridine was extruded at $220 \text{ }^\circ\text{C}$. Thermostabilization required a heating rate of $0.2 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ up to $240 \text{ }^\circ\text{C}$. Carbonization was performed at $1150 \text{ }^\circ\text{C}$ at $4 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. There is no register of the fiber mechanical properties obtained, albeit micrographs are available demonstrating the viability of the process [197].

Lin *et al* (2012) cooked cedar chips (softwood) with polyethylene glycol (PEG 400) and sulfuric acid. After isolation, lignin-PEG could be melt spun at $145 \text{ }^\circ\text{C} - 172 \text{ }^\circ\text{C}$. Fibers were thermostabilized at $250 \text{ }^\circ\text{C}$, held for 1 h, at $0.1 \text{ }^\circ\text{C} - 0.5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. All fibers melted. To overcome this problem, fibers were immersed in an aqueous solution of HCl for 2, 4 and 6 h to later be thermostabilized at $0.5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. As fibers could keep its integrity; carbonization was performed at $1000 \text{ }^\circ\text{C}$ using a heating rate of $3 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The fibers presented cracks over axial surface and porous over radial surface [135].

Chatterjee *et al* (2013) extracted hardwood lignin using organosolv procedure. Esterification was applied using dicarboxylic acid (phthalic, succinic, acetic and maleic) anhydride and THF as a solvent. Reaction was conducted at $70 \text{ }^\circ\text{C}$, under reflux, for 6 h. Acetylated lignins were extruded in a range of $153 \text{ }^\circ\text{C} - 158 \text{ }^\circ\text{C}$. Thermostabilization was carried out at $250 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Carbonization reached $800 \text{ }^\circ\text{C}$ using the same heating rate as thermostabilization. No mechanical property was given, solely structural micrographs. The authors suggest that fibers obtained could be used as adsorbent and anode materials for battery or supercapacitor applications [109].

Zhang and Ogale (2013) also used an acetylation procedure for commercial softwood lignin [198]. Different proportions of acetic anhydride, different reaction times and a fixed temperature of $85 \text{ }^\circ\text{C}$ were used. Best fiber could be obtained using 0.66 ml of anhydride per gram of lignin, taking 15 min to react. Differing from Eckert and Abdullah (2007), extrusion was obtained by dry spinning; thermostabilization was carried out the same way and carbonization used $1000 \text{ }^\circ\text{C}$ in a heating rate of $4.5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ [197]. According to the authors, the lignin-based carbon fiber obtained had the best tensile strength registered to date.

Souto (2014) extracted lignin from sugarcane using soda process. Esterification was performed, using octanoyl and lauroyl chlorides dissolved with pyridine. Neat lignin with no derivatization was also studied. Esterified lignins with octanoyl and lauroyl chlorides provided fibers at melting temperatures of $150 \text{ }^\circ\text{C}$ and $170 \text{ }^\circ\text{C}$, respectively, while neat lignin needed $250 \text{ }^\circ\text{C}$. All fibers were thermostabilized at $230 \text{ }^\circ\text{C}$ using a heating rate of $1 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. After, carbonization was conducted at $1000 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. No mechanical property was provided, only micrographs. Derivatization reduced melting temperature and favored morphological structure of the fibers obtained [199].

Adrianoycz *et al* (2014) registered a patent esterifying lignin with acid, acid anhydride, alkyl halide, or acyl halide prior to blending it to coal or petroleum based raw materials, in order to form precursor mixture and manufacture carbon fiber [200].

5. Technological process bottleneck

Many research institutes (FP Innovations, Georgia Tech, Innventia, ORNL, Institute for Textile Chemistry and Chemical Fibers, etc) and corporations (CIMV, GrafTech, Lignol Innovations, Sodra, Metso, Plasan Carbon Composites, etc) are integrated together in technology development to manufacture lignin-based carbon fiber. An example is the agreement between GrafTech and ORNL. They have already obtained results by melt-blown extrusion, forming a carbonized mat. Intentions are now concentrated to scale-up to market production [201]. Nevertheless, as commented before, Innventia dominated manufacturing lignin multifilaments fibers, using the lignin provided from LignoBoost[®] process [122].

It is noteworthy to mention that either LignoBoost[®] and Lignoforce[®] processes provide a lignin in a favorable condition, that is, in a high level of purity. These technologies are not applied to every industry, being in a wide process of expansion of their capacities [202]. Worldwide, paper and pulp industries always maximized lignin extraction from feedstock, not caring about structure preservation of the macromolecule, using it as fuel in boilers. The main objective of the whole industry was always to remove the lignin, as an uninteresting by-product. The challenge has been to convert this type of lignin (byproduct of the valorization process of the cellulose and hemicellulose) into carbon fiber.

Although the lignin fiber and the carbonized mat were obtained, they could be manufactured using a purified lignin from those specific technologies. And even so, the fibers provided from them have some limitations on their mechanical properties, restricting their applications. To widen application using available Kraft lignin from worldwide disposal, there are some technological bottlenecks that still remain, needing the research to overcome them. They are: (a) technical lignin variability, that depends on the feedstock, isolation and recovery processes; (b) feasible low cost purification process to reach the desirable levels required for extrusion; (c) softwood lignins must be converted/rendered to melt; and (d) green fibers are usually brittle and inflexible to be coiled and tensioned (mainly softwood lignins).

When the desired characteristics of the lignin are not completely understood, and there is a great variability of technical lignin (different sources, processes, isolation, etc), one can identify preferred properties, or the set of wanted parameters, in order to select them. This will be important when the availability of lignin increases because of biorefineries disposal. Another possibility is a selection or genetic modification in the plant to obtain a lignin with preferred characteristics. Selective extraction and recovery processes must be considered as an effort [166].

The desired price for lignin use as a precursor (ready for melt spinning) is US\$1.1/kg. This value was estimated using a purified lignin by FP Innovations' Lignoforce[®] in a completely matured process of purification [30]. However, some estimates show that to be suitable, the price of US\$1.52/kg (adjusted for a carbon fiber yield of 55%) would address the issue [30]. One must keep in mind that Lignoforce[®], Lignobost[®], etc, are 'recent technologies' abroad in development. Notwithstanding, if the purification process were implemented on technical lignin (thiolignin specifically) recovered from standard procedures, estimates would, roughly, be around US\$2.2/kg; which means that lignin as a precursor would cost close to US\$3.3/kg [8, 30, 94]. But even by that, lignin used as a precursor is still cheaper than textile grade PAN precursor, which costs between US\$4.4/kg and US\$13.2/kg (depending on oil price), or conventional PAN precursor (US\$11.1/kg, depending on oil price) [30]. This relevance of prices is not considered competitive and interesting industrially, because lignin-based carbon fiber is not comparable to PAN-based in terms of consistency. That is where these 'new technologies' (LignoBoost[®], LignoForce[®], Lignol[®], etc) appear as an actual feasible low-cost solution.

Low cost purification process could be reached more easily if industry experts were more collaborative and less conservative. There is a strong resistance to input processes at standard operation practice. The refusal comes from pulp and paper industries that resist implementing purification and refinery processes to lignin, when transporting it for this purpose would be costly. Even LignoBoost[®] was a challenge to be implemented, because industries, in general, do not feel comfortable to take risks in incipient technologies [30]. Few industries had modified their processes, were committed to providing a purified lignin, and then, overcame this hurdle (e.g. LignoBoost[®], Lignoforce[®], Biolignin[®], BioChoise[®], etc). But most industries are not included, limiting the market of readily available lignin to carbon fiber conversion.

The infusibility of softwoods lignin and the brittleness and inflexibility of the green fibers have gained great attention from researchers. This fact sparked interest for alternatives that circumvent these obstacles. They are mainly concentrated on blending, filler and derivatization as a way to overcome difficulties or even to promote

desired, or better properties. Although LignoBoost softwood lignins are ready for melt-spinning, herein the limitation is about standard processes under development.

Stabilization time could be cited as a challenge as well, although plasma procedure has been presenting an interesting effort to by-pass this barrier.

Some gaps still need to be investigated and others optimized. For example, the exact range of molecular weight that is required for an adequate extrusion is unknown. It is known that some polydispersity is required as mentioned before, but how wide must the distribution be and what fractions of molecular weight are required is still a doubt. Another topic to explore is an optimization on the structure parameters (e.g. phenolic hydroxyls versus alcohol hydroxyls) as cited earlier: it is known what chemical groups are desired or not, so an investigation in order to gather these functions to favor the extrusion step can improve the final product.

6. Final remarks

Lignin conversion into carbon fiber is feasible but it still requires improvements, mainly to those lignins provided using standard procedures (e.g. Kraft process). With a sustainable appeal, its use presents several advantages related to the current commercial precursor. These advantages are not restricted to the friendly environment approach, but also to production line benefits, and a rentable manufacture process.

Lignin-based carbon fiber is less-energy intensive and emits around 22% less CO₂-equivalent greenhouse gas emission than conventional PAN-based carbon fiber [203]. Besides that, production line is quite faster and environmental toxicity is lower. According to some research from ORNL, it has estimated a reduction of 30% to 40% of finished carbon fiber production cost.

For a feasible application on melt spinning, lignin must be purified (removal of contaminants) and fractionated (molecular weight control). Mostly softwood lignins are known to char instead of melt, because of their chemical structure. Many researchers are trying to overcome this difficulty, besides searching for improvements on hardwood lignins. These improvements involve structural modification, blending, filler or a mixture of them. Some results have pointed to an assertive methodology, but most of these are too costly and have been aborted for commercial use. Studies are still ongoing.

Special attention on future research should be concentrated on a set of desired properties that the material may have. Currently the knowledge of the so-called 'operational parameters' has made melt-spinning lignin feasible. However, adding this understanding with the expertise of the 'structure parameters' seems to be the hint to improve the fluidity of melt-spinning lignin, besides adding favorable conditions to reach an end-fiber with better mechanical properties. For example, it is known that high concentrations of phenol hydroxyls and aliphatic hydroxyl improves and hinders the fusibility, respectively. Molecular weight and polydispersity also have an open approach to be explored, where the correct parameters must be found. Condensed linkages must be avoided and β -O-4' linkage should be increased. When there is some resistance implementing modifications during the extraction processes on the plants, an optimization on the recovery process could be a good hint to achieve these desired parameters. Zhu (2013) investigated the influence of the pH, temperature and ionic force of the black liquor on the recovery of the lignin concluding that these parameters affect not only its purity but also its hydroxyls amount [84, 204]. Šurina *et al* (2015) evaluated the acid concentration to achieve the correct pH of the lignin precipitation (from the black liquor) and observed the same situation [205]. Hosseinaei *et al* (2016), Hosseinaei *et al* (2017) and Li *et al* (2017), as cited before, even observed that different sources, different conditioning temperature and further treatment could provide different amounts of hydroxyls groups, condensed bounds, β -O-4' bound, molecular weight and carbonyl [46, 136, 142]. Perhaps a survey over the recovery parameters of the lignin can help improve a better pathway to work with the macromolecule.

It should also be noted that the correct understanding about thermal conditions (during melt-spinning, thermostabilization, carbonization and graphitization) makes the difference. Each material may have an optimal temperature during thermal steps, besides the correct heating rate. The degradation temperature on melt-spinning must be avoided. Thermal treatments are the most important parameters on carbon fibers manufacturing. Thus, understanding the mechanisms involved and adding the correct set of structural parameters (which are responsible for thermal mobility) considerably improve the fiber production with high properties. Even the ratio of syringyl and guaiacyl, that also affects thermal mobility and mechanical properties, is correlated to these structural parameters.

Many researchers use defined temperatures to thermostabilize (generally 250 °C) or carbonize the fibers (generally 1000 °C), which depending on the set of physical-chemical conditions of the lignin, better conditions can lead to better results. These misguided temperatures were optimized for PAN-based carbon fiber and should not be applied to lignin, as the thermal-chemical mechanism involved in the conversion are completely different.

Currently, the automotive industry accounts for less than 1% of world carbon fiber output [203], but the trend is to increase this number. Carbon fibers-reinforced composites are known to be up to 35% lighter than aluminum and 60% lighter than steel. In a time when government policies have required a reduction of exhaust emissions from cars, replacement of automotive components for weight reduction is presented as an interesting alternative. For a long time, carbon fibers were not considered as a hypothesis because of their cost; however, lignin-based carbon fiber has been proven to be a solution to overcome this limitation. Considering the mechanical properties obtained so far, the automotive industry is considered the best segment market to introduce lignin-based carbon fibers.

To the extent that carbon fiber demand has grown worldwide, the availability of lignin has also increased. This is because of the emergence of biorefineries that, in addition to providing greater availability, it will do it in favorable conditions (e.g. less contaminants, more preserved).

Although several challenges must be overcome, lignin-based carbon fiber can be produced nowadays under limited mechanical properties. But this is quite enough to attend to some segments that are not restricted to the automotive industry. Efforts are ongoing to improve fiber quality, mobilizing many research institutes and corporations (e.g. Plasan, Ford Motor, BASF & SGL, DowAska, Kessler Research Team, Advanced Fibrous Materials Laboratory, GrafTech, ORNL and so on).

Lignin-based carbon fiber has emerged as a material with high technological impact, economically attractive, and environmentally sustainable which has great potential for market insertion. It is still far from being competitive with current precursors, but it shows signs of becoming a viable substitute in certain application areas, mainly the automotive market and those low-cost segments of the market, but with high demand.

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ORCID iDs

Felipe Souto  <https://orcid.org/0000-0002-2442-2836>

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