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Review

A Review on Lignin-Based Carbon Fibres for Carbon Footprint Reduction

Victoria Dumebi Obasa [1,*], Oludolapo Akanni Olanrewaju [2], Oluwashina Phillips Gbenebor [3], Ezenwanyi Fidelia Ochulor [3], Cletus Chiosa Odili [3], Yetunde Oyebolaji Abiodun [4] and Samson Oluropo Adeosun [2,3]

[1] Department of Mechanical Engineering, Edo State University, Uzairue, Iyamho 312107, Nigeria
[2] Department of Industrial Engineering, Durban University of Technology, Durban 4000, South Africa
[3] Department of Metallurgical and Materials Engineering, University of Lagos, Lagos 101017, Nigeria
[4] Department of Civil and Environmental Engineering, University of Lagos, Lagos 101017, Nigeria
* Correspondence: obasa.victoria@edouniversity.edu.ng

Abstract: Carbon fibers (CFs) are made mostly from a non-environmentally friendly polyacrylonitrile (PAN) and little from rayon. PAN-based CFs, require huge amount of energy for its production aside its contributions to the global CO_2 emission. Therefore, there is recourse to a more environmentally friendly sources of CFs biomass. Recently lignin has been recognized as a potential renewable raw material for carbon fibers to replace PAN-based. The magnitude and quality of CO_2 emission of lignin-based CFs are dependent on the processing route. On this premise; this review examines the various lignin-based CFs processing route adopted by researcher in the recent past to establish the most viable route with minimum carbon footprint emission. Outcome of the review shows that the major advantages of aromatic polymer (AP) generated precursor over PAN is the presence of higher quantity of guaiacyl units and oxygen content which makes the stabilization phase efficient and faster requiring less energy. Though there are several methods and options for the various stages of conversion of lignocellulosic biomass into CFs as highlighted in the study, establishing an optimum processing route will be a trade-off amongst various issues of concern; carcinogenic risk, carbon footprint emission, CFs Yield and mechanical strength of the CFs. Inferences from the study shows that the L-CF significantly produced reduced climatic impact in terms of CO_2 emission.

Keywords: biomass; fossil; carbon fibres; CO_2; processing route; environmental impact

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1. Introduction

The need to mitigate the accelerating pernicious effect of greenhouse gas (GHG) on our environment, has consistently provoked research towards discovering viable alternatives and substitutes to all human activities and applications that engender emission of CO_2 gas and other toxins that contends with the biosphere. Most studies have highlighted a major strategy of "light weighting" [1,2] as a possible remedy to multidimensional problem of carbon footprint. Lighting the weight of vehicles and other heavy-duty machineries invariably will reduce energy consumption [3]. This can be achieved by replacing conventional materials, such as heavy weight metals, steel, titanium and even polymer such as polyester, vinyl ester, nylon and graphite fibres that hitherto have been used in primary and secondary structural applications due to their high strength with bio-based materials [4,5].

Carbon fibres (CFs) are polymeric materials composed solely of carbon atoms. In comparison to steel, CF is five times stronger, more rigid, and even lighter. Owning to variable availability in divers form and vast characteristics, CFs have gained a wide range of applicability in areas like automobiles, aviation, sports, construction and medical devices where it is used for fabrication of products like bike frames, aircrafts wings, automotive drive shafts, tubing, containers, propeller blades, and car components [6,7]. Carbon fibre reinforced polymer (CFRP) is known to be lighter and stiffer culminating into higher fuel saving capacity. The eventual environmental impact of this composite is determined by life cycle assessment (LCA) [8,9]. LCA is a criterion used to evaluate the total life cycle of a product right from its extraction, processing through to its final waste management [10,11]. Thus, the environmental profitability of CFs is not just dependent on its performance in service but inclusive of the environmental concerns associated with its manufacturing processes. There are just few sources of synthetic raw materials for CFs such as PAN, pitch rayon, and resins. The scarcity of these resources coupled with the non-renewability accounts for the high cost of synthetically derived CFs. PAN-based CFs constitute 90% of yearly demand of CFs by several companies while pitch-based is about 10% [12]. This defines PAN as the most popular source of fossil-based CFs whose production route still contributes to the initial concern of GHG rather than solving the problem [13].This environmental concerns and high cost of PAN based CFs underscores it unique performance thereby necessitating a search for alternate biomass-derived precursors such as lignin, rayon, glycerol, cellulose and lignocellulosic sugars with a more environmentally friendly processing route that limits the evolution GHG [12,14,15].

Lignin due to its aromatic backbone with high carbon content of 60% has been regarded as a qualified source for CF production, though it is not the only natural polymer that may be converted into CF. The carbonization yields of about 40–50% as compared to 10–30% carbonization yields of cellulose a potential competitor makes lignin the more attractive option for economical processing [16–18]. However, another trait of lignin is that certain of its structures present thermoplastic characteristics that allow its extrusion via melt-spinning. Lignin is a polymeric constituent of the plant cell wall that provides supportive and impermeability functions in the vascular tissue and plays a role in defense against pathogens. Lignin is water-insoluble with long chain heterogeneous polymer composed largely of phenylpropane units, which are commonly linked by ether bonds. The conversion of cellulose and hemicellulose into fuels and chemicals leaves lignin as a byproduct [19–22].

Of all the proposed bio-based alternatives, lignin stands out as the world's largest natural AP and accounts for approximately 30% of the organic carbon in the biosphere [23–28]. Thus, lignin has been deemed a potential renewable raw material for replacement of polyacrylonitrile [29–31]. Notwithstanding, ascertaining the overall environmental impact of this potential replacement is crucial, consequent on the fact that lignin CFs processing route is very significant in the extent of carbon footprint emission. Also, biomass typically contains a significant amount of ash/minerals, which particularly is deleterious for the tensile strength of the resulting CFs, as these minerals lead to defects within the fibers. On this premises, this review examines the various processing routes adopted by researchers in the recent past to establish the most viable processing route for lignin- based CFs with minimum environmental consequence. The subsequent sections would consider the primary sources of lignin with their associated structures, the processing route for lignin generated CFs from the base material to the final product.

2. Sources and Structure of Bio-Based Lignin

2.1. Possible Sources of Biobased Lignin

From literature, there are more than 250 verified sources of biomass for lignin extraction. Some of these include; hardwood, softwoods, grasses, agro-industrial wastes such as brewery spent grains, sugarcane, bagasse and others as contained in Table 1. Despite these large reserves of potential CF bio-materials only about 20% have been explored. Thus, about 80% of these resources is grossly underutilized [32]. Though, there exist variable sources of biomass, the choice of base material for CFs production requires caution and knowledge of properties/structural linkages and composition of the biomass. Since the success of processing of lignin into CFs has a direct bearing with these parameters. The physical, chemical, and thermal properties of generated lignin depend on the monomer units (phenol-type compounds (H), guaiacyl-type compounds (G), syringol-type compounds (S), and catechol-type compounds (Ca), functional groups, molecular weight, degree of branching, and purity of the extracted lignin [33].

Table 1. Sources of Biomass with percentage composition of lignin and monomers.

S/N	Biomass	% Lignin	Monomer (H, G, S & CA)	References
1	Jute Stem	12–26	G and S	[33]
2	Hazelnut (HL) and walnut (WL) shells (Agro-food lignin)	85–95	H, G, S & CA	[34]
3	Piceabies wood	25–29	H, G & S	[34]
4	Pinus pinaster wood	23–30	H, G & S	[35]
5	Pinus pinaster bark	33	H, G & S	[35]
6	Phloem	38	H, G & S	[36]
7	Sapwood	32	H, G &S	[36]
8	Sugarcane bagasse	21	H, G & S	[37]
9	Wheat straw	22	G & S	[38]
10	Bambo	25–27	H, G & S	[39]

2.2. Structure of Biobased Lignin

Lignin is a heterogeneous aromatic polymer mainly constituted by three precursors: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Although, its molecular structure can vary significantly, lignin is an amorphous and cross-linked polymer in its natural occurring state. This precursor is often mentioned as phenylpropane or C_9 units, where the hydroxyl group is linked to the C_4 and substitutions with one or two methoxyl groups may be present at the C_3 and C_5. Thus, the aromatic ring of the three alcohols is called *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) if the ring is unmethoxylated [40,41]. Guaiacyl is found predominately in softwood lignins, syringyl is found in hardwood lignins, and phydroxyphenyl occurs mostly in annual crops. The typical chemical structure of cellulose, is illustrated in Figure 1. The linkages in lignin appear to be randomly distributed [42]. Approximately two-thirds of the linkages are ether linkages and approximately one-third are carbon-carbon linkages [43]. The carbon-carbon bonds are generally more stable compared to the ether bonds and are often resistant to processes such as chemical pulping.

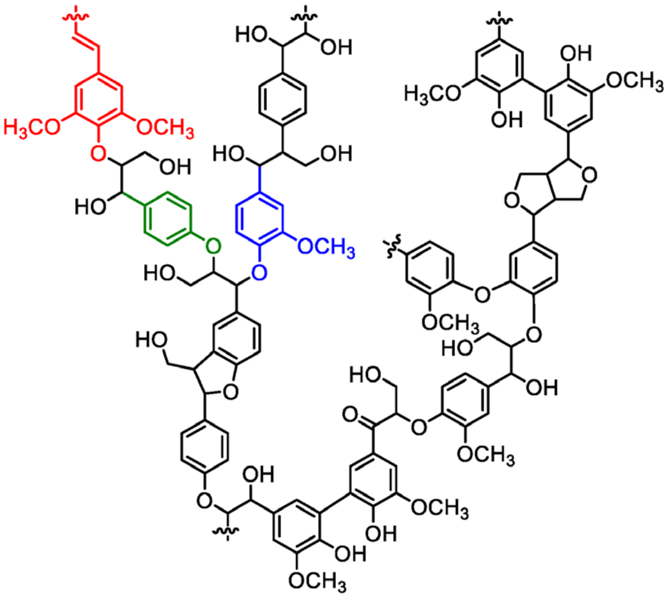

Figure 1. Chemical structures of the primary lignin precursors (a) and the hydroxycinnamates (b) R = H. Adapted from [44].

3. CFs Processing Route

The transformation of biomass into CFs involves well defined route as illustrated in Figure 2. It starts with (i) preparation of raw material (ii) extraction of organic precursor (iii) derivation of precursor fibres (iv) stabilization of CFs precursor (v) carbonization of CFs and finally (vi) adapting CFs for specific application. After the fibers have been produced, the composites can be manufactured. This is done by arranging the fibers in an application-specific way and adding a polymer matrix. The composites are then formed using injection molding, compression molding, or resin transfer molding [42,45] Thus, a single-step process for converting biomass does not exist.

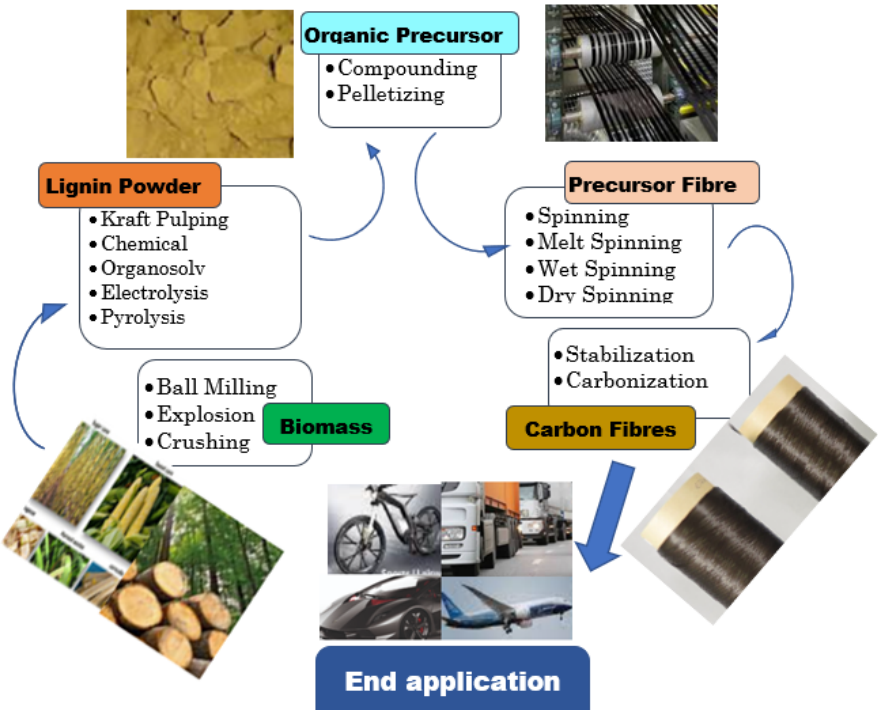

Figure 2. The conceptual flowchart of Lignin- based carbon fibre Processing Route through to end application.

3.1. Material Preparation

This step varies depending on the source of biomass under consideration. For wood lignin, ball milling or vibratory milling could be employed for reduction of biomass into sizeable particles or chips for ease of extraction [46]. Also, for wooden biomass steam explosion could be employed. Steam explosion process involves heating of the wood biomass in the presence of steam to between 200–220 °C followed by rapid decompression. The wood is "exploded" and individual fibers and fiber bundles are formed. From hardwoods, a subsequent extraction with organic solvent follows [47] While for agro-based lignin (crops) the biomass is exposed to the atmosphere for couples of weeks to make room for natural degradation before eventual crushing the biomass into manageable particles ranging from mm to µm [48].

3.2. Conversion of Biomass to CFS Precursor

Separation of lignin from its celluloselistic fibres as mutually contained in the base bio-material is crucial as the various processing technique impacts directly or indirectly on further processibility of the obtained precursor into finished CF. This section X-rays the environmental impact, the yield and economy of various pulping methods reported in literature. Methods such as chemical pulping, electrolysis, pyrolysis and solvolysis (combination of organic and inorganic acid) etc., have been employed in the past for the recovery of lignin from source [18,49].

Chemical Pulping is one of the oldest pulping methods that originated from Sweden about 130 years ago [50,51]. It's quite expansive as it involves the use of both organic chemical and inorganic chemical to isolate lignin from cellulose. Inorganic chemical such as caustic soda or sodium sulphide in aqueous solution act as reactant in the digester. The alkali medium breaks down the crossed linked chain of lignin and cellulose usually present in non-wood materials (wheat straw, rice straw) mostly in annual crops [52,53]. This entire process known as kraft pulping successfully disband phenolic hydroxyl groups characteristic of non-wood lignin. Upon separation, the resulting cellulose is further treated for the production of paper. The Kraft pulping process is challenged with complete or partial plugging of the filter cake and/or of the filter medium [54,55]. This blockage changes lignin solubility while it induces a high pH level and this consequently brings about restructuring of the lignin particle. In effect, the emerging CFs precursor still retained significant amount of ash, which is deleterious to the strength property of the generated CFs precursor.

An enhancement over this traditional method was the introduction of the lignoboost process [56]. Instead of direct washing of lignin obtained from black liquor evaporation plant as in the case of the traditional method, it is further re-dispersed in an acidic medium usually CO_2 before the final washing is done. Figure 3 is a comparison of the process route for traditional kraft pulping and the lignoboost. The encircled process shows enhancement of this current method over the conventional kraft pulping process. Evaluation of the process showed an improvement in the economy of the production, increase yield and about 0.2% reduction in ash content was achieved. Klett et al. [57] used hot aqueous acetic acid to purify and fractionate black liquor resulting in an "ultrapure" lignin with an ash content lower than 0.1 wt.%. This in turn culminates to an overall increment in strength of extract.

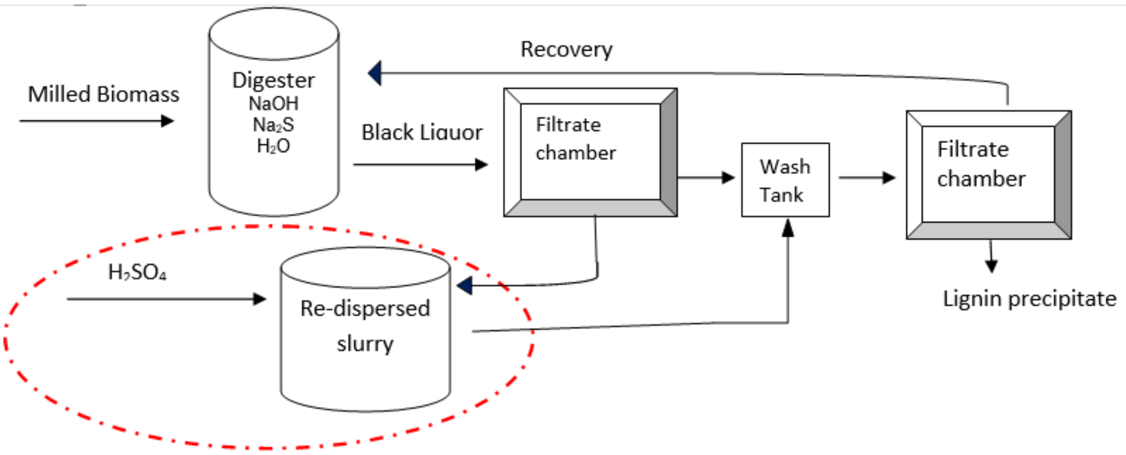

Figure 3. Simple layout of improved kraft pulping process (lignoboost).

The variation of kraft pulping using inorganic acid, though efficient in terms of yield is plague with environmental concerns such as release of waste water (black liquor) containing sulphur contaminants [11]. Traces of sulphur are still evident in the extracted precursor, which are potential sites for imperfection. In response to this problem several organic chemicals like alcohol have been used to recover a purer lignin precursor through a more environmental procedure. However, the use of alcohol as organic solvent is limited due to its low boiling point. This is because it necessitates the use of a high operating pressure that can only be achieved using special equipment that is expensive to purchase and operate. Hence, alternative organic solvents such as glycols, phenols, esters, organic acids, acetone and amines are used with less complexity.

Organosolv is a pulping route that uses an organic solvent to solubilise lignin and hemicellulose. It has several advantages when compared to other popular methods such as kraft or sulphite pulping. Organosolv lignin has higher purity. A lot of works has been conducted in this regard to show that this method wields some edge over kraft process as its more economical, has increased brightness for the pulps, higher yields, without bad smells and with less effluents than conventional processes [46,58]. Despite these merits of this process, it still has some drawbacks in terms of high cost of production and inapplicability to softwood.

Electrolysis of kraft black liquor (BL) is another advancement over the conventional Kraft and organosolv process for energy and lignin recovery. Study has it that introduction of this idea has economic and environmental advantages, as it simultaneously generates valorized lignin precursor at the anode and a clean hydrogen gas at the cathode [49]. Here Platinum (Pt), nickel (Ni), and AISI 304 stainless steel (SS) are suitable for use as anodes and cathodes. This method seems efficient and has minimal environmental concern as hydrogen is seen as an uncontaminated fuel since its ignition only produces water and energy [59,60]. It is the lightest fuel and the richest in terms of energy per mass, and it has a very high higher heating value, about three times higher than that of gasoline [61]. The increasing energy costs coupled with stringent environmental regulations have led to a great interest on the hydrogen economy [62]. Also, hydrogen is used in a wide range of industrial processes, such as in refining, methanol production, glass industry and metallurgy and as fuel for rocket engines [63]. The emerging lignin is further dried, pulverized, pelletized for storage and further production of precursor fibres.

3.3. Conversion of Organic Precursor (Lignin) to Precursor Fibres

Basically, the conversion of organic precursor into precursor fibre is by spinning process. Spinning process is an inevitable step in CFs production. It transforms ground precursor into continuous fibers. Unlike polymers, lignin as a bio-based CFs precursor cannot be readily extruded into precursor fibres owing to its thermoplasticity [55]. Spinning of softwood-based lignin has been demonstrated to be very difficult [64]. However, the blending with polymer or some quantities of cellulose have been reported to be very effective in improving the spinnability [65,66]. Three major techniques for spinning are available in literature namely melt, wet and dry spinning depending on the raw material properties. In melt spinning, the precursor is heated in high temperature and melt first. Then it will be extruded through a spinneret containing small capillaries, and finally the fibers will be produced. On the other hand, wet spinning involves, extracting a concentrated solution of the precursor through a spinneret into a coagulation bath; precursor is easier to precipitate and form into a fiber when produced by the spinneret as the solvent is more soluble in the coagulation fluid. In dry spinning technique, fiber forms by evaporating the solvent in a drying chamber [67,68]. Commercial CFs for primary structural application are usually spun in a continuous pattern. The continuity in this fibre is the desirable strength factor. In contrast, cases of carbon fibres with discontinuous or randomly aligned filaments find use in nonstructural (or secondary structural) applications as nanofibers or mats [18].

Most thermoplastic materials employ melt spinning due to their shear thinning characteristics. The major merits of melt-spinning over other spinning techniques are its environmental friendliness and high yield attributed to the fact that it does not involve the use of solvent. Some of the drawbacks of melt spinning is the need for high level of reactivity that ensure adequate crosslinking in subsequent stabilization and carbonization [69]. Nordstrom et al. (2013) [64] investigated selected grades of softwood kraft lignin (SKL) and hardwood kraft lignin extracted by the lignoboost process. Both lignins precursor were successfully melt-spun into precursor fibers because of the removal of large molecular weight fractions by ultrafiltration. Using the fractionated SKL, the stabilization step could be completed within 45 min (heating rate of 158 °C/min [70], which is among fastest so far.

3.4. Impact of Spun PFs Diameter on CFs

Recent studies have shown that diameter of spun PFs have significant effect on the tensile properties of CFs. It has been established that the fibre diameter has inverse relationship to strength of the fibre; the smaller the fibre diameter the less possibility of flaw, hence the more the strength of the fibre. Stretching of filaments provides high molecular orientation and better mechanical properties [47]. Andreas et al. [67] investigated the stabilization conditions and the impact of spun PFs diameter for CF made from dry-jet wet spun lignin and cellulose blends (ratio 70:30) of softwood kraft lignin (SKL) and fully bleached softwood kraft pulp (KP). Two major fibre diameters: 22 µm (thick) and 14 µm (thin) of PFs were produced. The increased draw ratio in the fiber spinning combined with a reduced PF-diameter [7] resulted in CFs with a tensile modulus of 76 GPa and tensile strength of 1070 MPa. Preparing CFs by dry-jet wet spinning of unfractionated SKL and paper-grade KP blends is a very promising route for making cost-efficient CFs. Considering a holding time of 2 h at 250 °C during the stabilization, results revealed that the PFs can either be oxidatively stabilized in less than 2 h or instantly carbonized. After 5 h of isothermal treatment at 250 °C, no difference between the fast and slow heating rate was observed thereby ruling out the necessity of very slow heating rate as previously practiced [71]. A statistical analysis by Gellerstedt et al. [47] in Figure 4 investigated strength properties of different lignin precursors. Data obtained from the investigation further explains the inverse variation of the mechanical properties of CFs with the spun diameter of precursor fibre from source [72]. From Figure 4 it can be clearly seen that the PF with the largest diameter (84 µm) has the lowest strength 26 MPa.

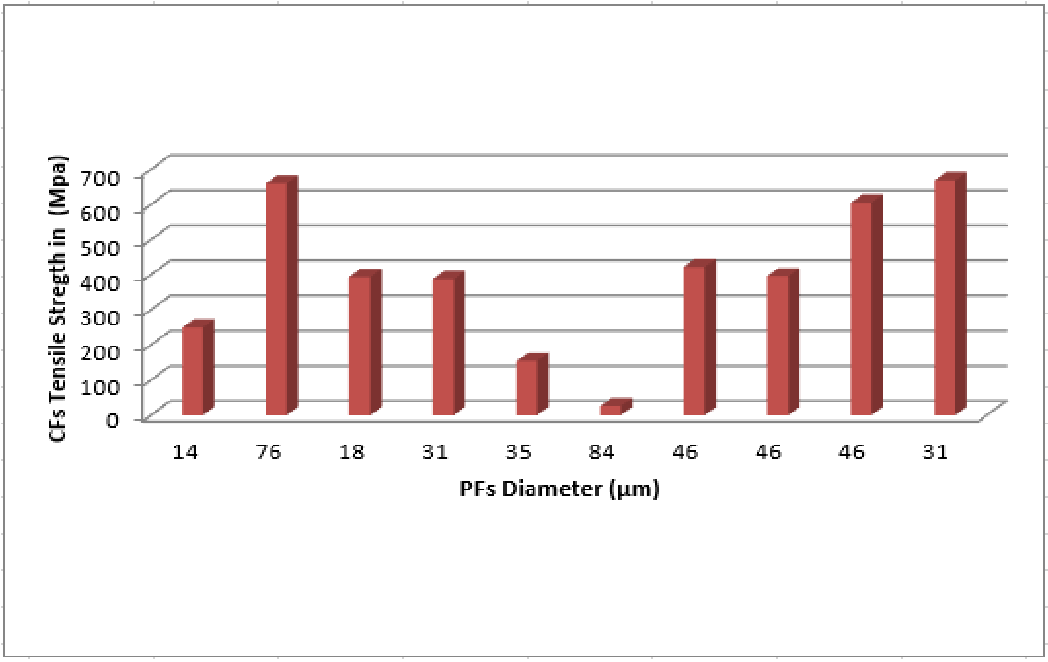

Figure 4. Variation of Strength Property of CFs with PFs Diameter.

3.5. Conversion Precursor Fibres (PFs) to Carbon Fibres (CFs)

Transition from precursor fibre to the final desired product (carbon fibre) entails two critical steps, stabilization and carbonization. This stage is critical in that it stipulates the level of energy consumption and processing time, which in turn defines the viability of the processing route. Minimum energy consumption during this process culminates into less emission of carbon footprint and vise versal. This section explores viability of various method that have been used for stabilization as well as carbonization. The use of lignin instead of the traditional raw material PAN presents a renewable raw material source. Also, lignin also possesses other unique properties in terms of its chemical structure, which makes it suitable for carbon fiber production. The oxygenated nature and huge content of aromatic compounds consequently reduce energy use in the carbonization and stabilization steps when compared to PAN [73–75].

3.6. Stabilization Process

Stabilization process induces thermosetting behaviour on the precursor fibre ensuring adequate cross- linking and fusing of the fibre [76]. The popularly used oxidative stabilization method is usually carried out at a very slow temperature with an amplified oxidising environment [77]. Summarily the impact of oxidative stabilization on fibre is dependent on the level of oxidant, temperature and time. Difference in stabilization behaviour of various PFs can be attributed to the difference in structure between softwood and hardwood. Softwood kraft lignin (SKL) possesses a more branched and cross-linked structure as compared with hardwood kraft lignin (HKL) [78]. Also, the quantity of guaiacyl units is higher than HKL, leading to a faster stabilization step for SKL. Furthermore, in comparison with petroleum pitch and PAN, SKL has a higher oxygen content, which may be sufficient for stabilization using only heat [79]. One of the greatest challenges of this procedure is attaining homogenous stabilization throughout the entire fibre especially for pitch-based fibres. It has been observed that the development of skin-core structure prevents oxygen from penetrating deeper into the structure [80]. This phenomenon is caused by the competition of chemical reactions on the surface of the fibre and diffusion. To avert the formation of skin-core structures, a reduction in the reaction temperature and/or an increase in the oxygen partial pressure are necessary steps to the kinetics of oxidative stabilization [81–83]. Using a large diameter fibre has also been suggested to have a negative impact on the skin-core structure because of the relatively limited penetration of oxygen into the pitch fibre.

Microwave heating is one of such way to decrease energy consumption and other associated challenges encountered during stabilization. It works based on the principle of electromagnetic field attraction and dielectric properties of materials. The major occurrences during the process are radical, oxidation, condensation, rearrangement reactions and dehydration [84]. Carbon fibres, which have high dielectric loss factors are known to be reflectors of microwaves; consequently, they have a low penetration depth of microwaves [85]. It is efficient in that the heat energy within the system is directly concentrated on the precursor fibre unlike the conventional pyrolysis in which the supplied energy is directed towards heating up the entire furnace and the precursor fibre resulting in higher energy consumption. The microwave stabilization techniques are advantageous over other conventional heating process due to use of smaller equipment, short processing time and lower energy consumption [86]. Adoption of a more compact equipment, in this new technology slashes energy consumption by approximately 50% and offers a substantial reduction in processing time compared with the conventional method, which utilizes oxidation ovens heated from 200° to 300 °C and carbonization furnaces maintained at 1000° to 2000 °C.

The experiment of Wei et al. [82] focused on minimizing the stabilization and graphitization time, which is germane in CF manufacturing. The effect of stabilization conditions on chemical structure, yield, microstructure and mechanical properties was considered. A graphitization time of 180 s and microwave power of 800 W, equivalent to the temperature of 2100 °C, a high graphitization degree ($R = 0.61$) was observed and the crystallite size was as large as 5.10 nm, which are better than that of M40J and T800H. Subsequent to 5 min treatment, the average tensile modulus of samples actually increased by 23% from 189 GPa to 245 GPa. Invariably, the results obtained from this work showed that the microwave plasma is an efficient route for the development of carbon fibers with good microstructure and high graphitization degree. This is incongruence with finding reported earlier [67].

4. The Environmental Impact of Production Route of Fossil Based and Bio-Based CFs

The persistent growth of carbon footprint in the transport sector has awoken the consciousness of both transport and climate change policymakers. Greenhouse gas (GHG) emissions from transportation account for about 27 percent of total U.S. greenhouse gas emissions, making it the largest contributor of U.S. GHG emissions. Between 1990 and 2020 [87], GHG emissions in the transportation sector increased more in absolute terms than any other sector. A European Environment Agency model projected two possible occurrences by 2030 [88]. If necessary, measures such as a shift towards low or non-carbon fuels and light weighing are maintained then, a significant reduction in CO_2 emissions by 11% is achievable but if otherwise the increment in CO_2 emission will be in geometric progression. Several studies also confirmed that transport sector CO_2 emissions steadily increased over the last ten years despite significant efforts to cut them in some countries [89,90].

The use of natural fibre reinforced polymer (NFRP) to mitigate against carbon footprints can be tied to carbon sequestration from cradle through to grave of the lignin product. Production of lignin as a bio-based materials for CFs starts with agricultural cultivation, which engenders photosynthesis. During this process, the plant absorbs carbon dioxide from the atmosphere while releasing oxygen as an output, i.e., carbon sequestration [91]. The overall process is enabled by solar energy from renewable source that are in abundance. This is clearly a reversal of GHG emissions, reducing harmful global warming. In stark contrast with the extraction of raw materials for CFs from synthetic source which emits large amounts of carbon dioxide into the atmosphere; a significant contributor to climate change. It is by virtue of the lower carbon emissions and lower scores from other EI categories that bio-based materials have received such significant attention in recent years [92].

Processing of cultivated biomass is one key that influences the magnitude of NRFP contribution to GHG emission. Fibre preparation and fibre treatment could represent a large proportion of the processing emissions [93]. Any treatments at this stage will increase the EI and economic cost, due to the production and application of these chemicals. However, LCAs demonstrate that no method is more efficient overall, and that any use of chemicals significantly negatively affected the EI score. It was also noted that, in particular, the lack of technological development in processing methods is seen as the decisively limiting factor for the natural fibre industry in Europe.

Aromatic Polymer (AP) fibres can transform into CFs without a gas-phase stabilization step in the manufacturing route, which is an inevitable step in production of fossil-based CFs. This step has been reported to consumes about 48% of the energy needed for production of PAN CFs [94]. AP are known for large-tow (LT) as they carbonize more readily and possesses a high flame resistance property that prevents them from melting during the carbonization process. Sequel to this unique attribute, APs are deemed more suitable and cost effective than PAN [95] subject to the processing technique as some of the production route like use of benzidine is associated with health issues. A recent review of 62 Scopus-based papers on environmental impact of lignin-based product [96] revealed that CFs derived from lignin resulted in 22% fewer GHG emissions than those derived from conventional PAN fibres.

Recently Sakamoto et al. [97] employed LCA tool to evaluated life cycle of CFs product from cradle-to-gate in relation to other associated products. The aim of the study was to estimate the GHG emissions of the production process of CFs manufactured from an AP and those manufactured from conventional PAN. Here, two production processes adopted for AP precursors are the classical benzidine method and the coupling method. Results deduced that these studies show that the GHG emissions from CFs from PAN were 31.00, 29.50, and 30.29 kg-CO_2 eq/kg, respectively. These estimates were consistent. GHG emissions from flame-resistant CFs were 21.12 kg-CO_2 eq/kg [8]. The GHG emissions from CFs from APs were 24.00, 25.35 from the APs with the classical benzidine method and 40.46 kg-CO_2 eq/kg from the APs with the coupling method. Also, a cradle-to gate consequential life cycle analysis (CLCA) by Khandelwal et al. [98] focused on GHG emissions reduction by replacement of fossil-based bitumen with lignin. Steam explosion and Lignoboost technology were adopted for lignin isolation. The end result of assessment revealed that using lignin has the potential of mitigating GHG emissions in the infrastructure sector by 18–27% for Kraft lignin and 9–20% for biorefinery lignin. A further projection into the future shows that there is a possibility of 32.8% CO_2 emission reduction by 2030. An LCA investigations by several other scholars affirmed the possible potentials of lignin to minimize the instance of emission GHG gases [77,99,100].

Tribot and co-authors understudied the Life Cycle Analysis (LCA) of four different Lignin extraction process to determine their EI. The investigation considered Kraft, organosolv, soda, and sulfite proceses [99]. The organosolv process presents the highest total potential environmental impact (PEI) as 0.25 kg-CO_2 eq/kg followed by the Kraft process with about 0.09 kg-CO_2 eq/kg, followed by the sulfite process having a value of 0.03 PEI per kg of lignin and finally, the soda process has the lowest pollution with PEI values of 0.02 kg-CO_2 eq/kg attributable to addition of anthraquinone (0.1%) that stabilizes hydrocelluloses and catalyzes delignification. The advantage of the soda process results in the absence of sulphur in the cooking products which is the major way to get a lignin purer than Kraft lignin. The details of EI contribution of each method are presented in Table 2. It is important to state that the wide variation in PEI values inferred by various authors is consequent upon the source of biomass used for the study.

Table 2. Contribution of process step carbon footprint.

S/N	Bio-Mass	Process	CO2,eq/kg	Reference
1	Softwood	Kraft process	2.9	[81]
2	Softwood	Kraft lignin	0.2–0.7	[17]
3	Softwood	Kraft process	0.09	[101]
4	Agro-based	organosolv	1.85	[102]
5	Spruce Bark	organosolv	1.4–2.1	[103]
6	Agro-based	organosolv	1.0–2.7	[99]
7	Softwood	organosolv	0.25	[101]
8	Agro-based	Lignoboost	0.55	[76]
9	Agro-based	Lignoboost	0.17	[100]
10	Softwood	Lignoboost	0.2–0.6	[104]
11	Softwood	Soda process	0.02	[101]
12	Soft Wood	sulfite process	0.03	[101]

In a cradle to gate life cycle assessment by Janssen et al. [75] using a functional unit 1 kg of lignin-CF produced from softwood lignin followed an attributional approach. Interestingly, the study considered improving and optimizing the lignin-CF production process from an environmental life cycle point-of-view by projecting an improved prospective production system by 2025 and comparing the EI of the L-CF production process with CFs from other synthetic sources of PAN-CF. Outcome of the assessment showed that the climate impact per kg of lignin-based carbon fibres produced was 1.50 kg CO_2,eq. in comparison to climate impact of fossil-based carbon fibres with value 38.9 kg CO_2,eq. this is about 96% higher than the impact of L-CF fibres.

Further study as highlighted in Table 2 show the contribution of each process steps towards EI while Figure 5 captured the sum total of various impact categories such as global warming, acidification eutrophication potential, photochemical ozone creation potential and human toxicity potential of L-CF in comparison with their fossil counterparts [73,105,106].

Das et al. [73] considered the use of LCF in carbon fibre reinforced polymers (CFRPs) and compared it with the use of PAN-CF. The author concluded that a 30% reduction in life cycle energy use could be obtained by switching from PAN-based to lignin-based fibre. However, it was assumed that lignin production did not lead to an environmental impact as it is a by-product of pulp or ethanol production. Similarly, a study [12] reported that energy use during carbonization of the precursor fibre is a main contributor to environmental impact, and that assessments of both lignin-based and recycled carbon fibre are subject to challenges regarding allocation of environmental impacts.

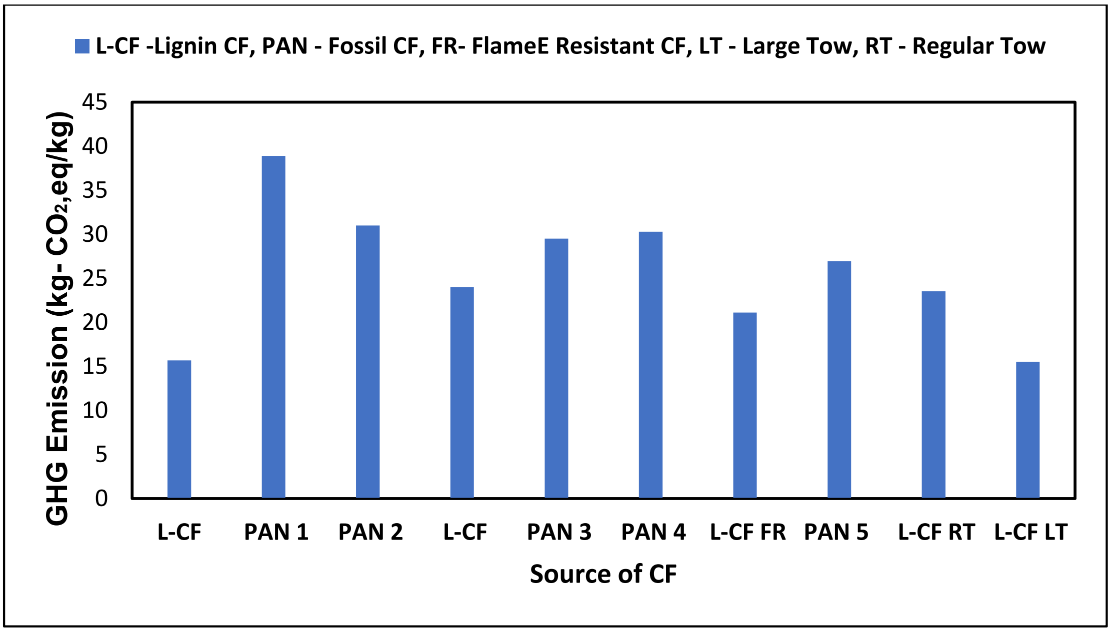

Figure 5. Comparison of GHG emissions from lignin-based CFs and PAN based CFs.

Also, Sakamoto [87] examined the GHG emissions from APs and PAN CFs. For the GHG emissions from the AP CFs two methods were presented; the classical method and coupling method. The GHG emissions of the entire CF production process were the sum of the GHG emissions from the precursor-fiber preparation and the CF production representative of both large tow (LT) and regular tow (RT). Finding shows that the GHG emissions from the CFs from PAN, from the APs (RT) and APs (LT) from the classical method, and from the APs from the coupling method were 26.94, 23.53, 15.53, and 40.68 kg-CO_2 eq/kg, respectively. Compared with the conventional PAN based CFs, GHG emissions from the AP CFs from the classical method (RT) were 11% lower, and those from the AP CFs from the classical method (LT) were 42% lower. GHG emissions from the AP precursors were 20.49 kg-CO_2 eq/kg and those from PAN were 10.08 kg-CO_2 eq/kg. Notably, the GHG emissions from the AP CFs through the CF production process were negligible owing to the fact that AP CFs do not require gas-phase stabilization during the CF production process, which is attributable to the flame resistance nature of the AP precursors [73–75,105,106].

5. Conclusions

From the foregoing review, the outstanding strength and modulus possessed by CFs derived from PAN (a synthetic, polymeric precursor) are their primary advantages. However, their high cost and environmental concerns during manufacturing serve as the primary concern for continued research for alternative precursors and processing routes. The use of lignin instead of the traditional raw material PAN does not only provide a renewable raw material source, but the lignin also has some other inherent properties that in principle, makes it a choice material for carbon fiber production. The large content of aromatic compounds (guaiacyl units) and the oxygenated nature of lignin reduces energy use in the carbonization and stabilization steps completely accounting for overall reduction in process time and energy efficiency.

There is a synergy between the level of GHG generated and the various stages of manufacturing involved, ranging from lignin extraction from biomass, conversion of base precursor to precursor fibre through to emergence of CFs via stabilization and carbonization processes. Consequently, with available processing options, this production route highlighted below are deemed to have minimal environmental impact; electrolysis for conversion of biomass into lignin, melt-spinning enhanced by ultrafiltration for conversion of base lignin to precursor fibres and microwave stabilization techniques for conversion of precursor fibres into carbon fibres.

- The electrolysis method of lignin extraction from biomass is an advance technique that produced a lignin with high level of purity as well as clean hydrogen gas output.
- The melt-spinning enhanced by ultrafiltration has been deemed the most efficient method for conversion of lignin to precursor fibres due to its environmental friendliness as it does not involve the use of solvent that result in carbon footprint emission.
- Microwave stabilization techniques are advantageous over other conventional heating process due to the use of smaller equipment, short processing time and lower energy consumption. Adoption of a more compact equipment, slashes energy consumption by approximately 50% and offers a substantial reduction in processing time.

Summarily, the irreversible alterations of the earth geographical features are traceable to the adverse effect of carbon footprint. Climate change encompasses not only the rising average temperatures but also extreme weather events, shifting wildlife populations and habitats, flooding, and a range of other impacts. The lignin processing routes are significant in determining the magnitude of carbon footprint emission in CFs production. It could further impact on its viability as potential replacement for PAN especially at the early stage of lignin extraction. Hence, adopting the most beneficial processing route is of interest in reducing the level of energy consumption and use of deleterious solvents, which eventually culminates into reduction in GHG emission.

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