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Lignin Carbon Fibres: Properties, Applications and Economic Efficiency

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Abstract

Lignin carbon fibres are cheaper than carbon fibres from petroleum sources but they are yet to meet the required performance for automotive applications. They supersede petroleum-based carbon fibres in terms of cost, light-weight, environmentally sustainability, availability and renewability. It is evident that the performance of lignin carbon fibres depends of their sources (include biomass type), and processing/treatments. To enhance the application of these fibres, there is need for in-depth understanding of the evolution of their properties considering their source, extraction method, and further processing. On the other hand, it is important to understand the driving factors in the economic efficiency of the carbon fibres. This will guide researchers and industrialist in the search for high performance lignin carbon fibres with acceptable economic efficiency.

9.1 Introduction

The quest for environmentally sustainable, renewable and economically attractive materials has rapidly increased in the past decades, due to the exponential increase in the world demand and application of various engineering materials. Carbon fibre reinforced polymer composites has outstanding essential properties for high performance applications such as aerospace, automobiles, marine and sports. Carbon fibres are highly demanded in these applications because of the need to reduce weight, minimize fuel consumption and improve environmental sustainability by reducing harmful emissions. Several studies have been conducted on industrial application of carbon fibres [1,2]. It has been forecasted that carbon fibre demand will increase exponentially in the coming years [3].

Attempt to reduce cost, energy expenditure and CO₂ emission has led to the introduction of lignin carbon fibres an alternative source of carbon fibres other than petroleum-based fibres. Lignin is obtained from biomass sources (hard and softwoods, wheat straw,

bagasse, bamboo, switch grass, etc.) [4,5]. Lignin is the second most abundant naturally available polymer after cellulose. It is the only renewable resource material containing aromatic rings making it a suitable carbon precursor [6,7]. The other important precursors are polyacrylonitrile (PAN) and mesophase pitch [8].

Lignin carbon materials find applications as structural materials for vehicles, graphite electrodes for arc furnaces, nanoporous carbon fibre for flexible high-performance supercapacitors, composite filter for heating, ventilation and air-conditioning (HVAC), filters for HVAC, CO₂ and VOC capture, H₂ storage, electro-catalyst for promoting chemical (hydrogen-oxygen) reactions as well as sustainable electrode materials. These tremendous advantages of lignin carbon fibre necessitate a better understanding of its properties for wider applications and higher economy efficiency. This chapter focuses on outstanding properties, applications and economy efficiency of lignin carbon fibre. Some existing and relevant economic or cost models on this renewable fibre are similarly reported.

9.2 Lignin carbon fibres

Increase in demand for reduction in weight, emissions, fuel consumption and cost efficiency in applications such as automotive, aviation and wind energy has created a turn from metallic to composite materials with carbon fibres. The use of carbon fibres is capable of reducing the component weight of automobiles up to 60% while maintaining the same functionality [9] (Figure 9.1). Fibres containing at least 92 wt. % carbon are referred to as carbon fibres whereas those containing at least 99 wt. % carbon are called graphite fibres [8]. They possess excellent electrical, mechanical, thermal properties and chemical stability. Carbon fibres are categorized based on their modulus of elasticity including;

- a) Low modulus fibres (40 - 200 GPa),
- b) Standard modulus (200 - 275 GPa),
- c) Intermediate modulus (275 - 345 GPa),
- d) High modulus (345 – 600 GPa) and
- e) Ultra-high modulus (600 – 965 GPa) fibres.

Carbon fibres are also classified according to their source including [10];

- a) PAN-based carbon fibres
- b) Pitch-based carbon fibres
- c) Mesophase pitch-based carbon fibres

- d) Isotropic pitch-based carbon fibres
- e) Rayon-based carbon fibres
- f) Gas-phase-grown carbon fibres
- g) Lignin based carbon fibres

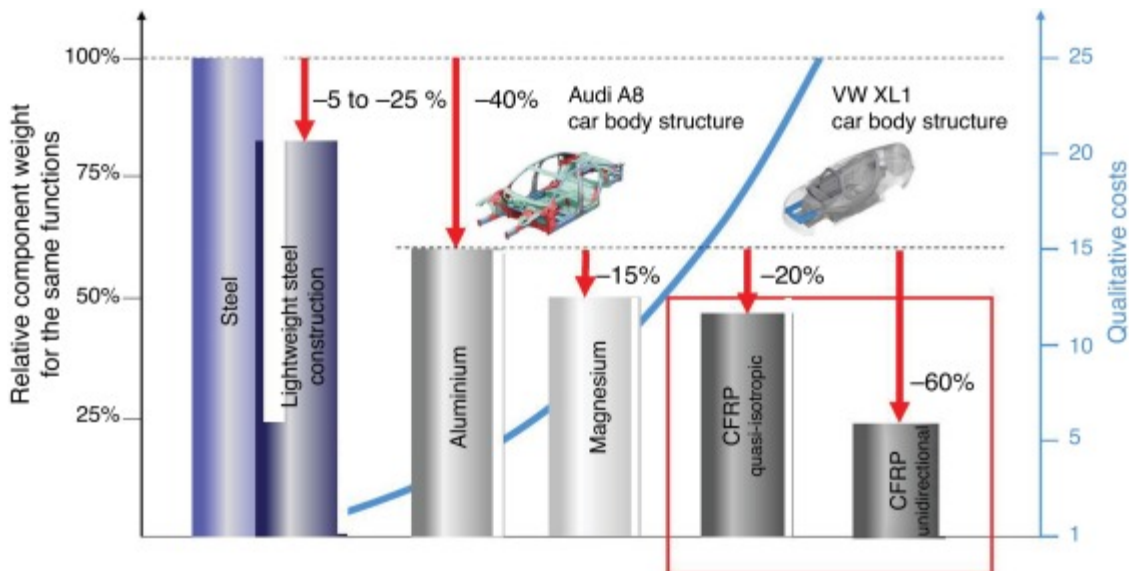


Figure 9.1: Potential of lightweight construction – material substitution in structural applications [11].

Another classification of carbon fibres is based on the heat treatment temperature including [10];

- a) Type-I, high-heat-treatment carbon fibres: These are fibres treated at final heat treatment temperature above 2000°C. They are associated with high-modulus type fibres.
- b) Type-II, intermediate-heat-treatment carbon: These are fibres heat treated at final temperatures around or above 1500°C. They are associated with high-strength type fibres.
- c) Type-III, low-heat-treatment carbon fibre: When the final heat treatment temperature is not greater than 1000°C. They are associated with low modulus and low strength fibres.

Lignin carbon fibres are attractive source of carbon fibres because they are economically attractive and, environmentally sustainable [12]. Lignin carbon fibres have the ability to reduce the cost of manufacturing by more than 80% [13] and are therefore considered an alternative for Pan based carbon fibres. Lignin is less expensive and, available in massive

quantities as a waste product in the paper industry and from bio refineries. Lignin is also renewable and sustainable. Carbon fibres have been obtained from lignin in reasonable quality and quantity by several research groups.

9.2.1 Properties of lignin carbon fibres

Quality assessment of carbon fibres are usually based on properties such as tensile strength, tensile or Young's modulus, electrical properties, absorption behaviour, thermal stability in the absence of oxygen, thermal expansion, chemical stability and density. For the assessment of suitability of lignin carbon fibres, attention is paid to tensile strength, elastic modulus, elongation and surface morphology. Tensile strength, modulus and elongation of individual carbon fibres are usually measured by single-filament testing, according to BS ISO 11566 or ASTM D3379-75 standards. Filaments up to 20 and above are tested and a statistical analysis conducted to determine the average [2,14]. The surface morphology and size of the fibres are usually measured using high resolution scanning electron microscope.

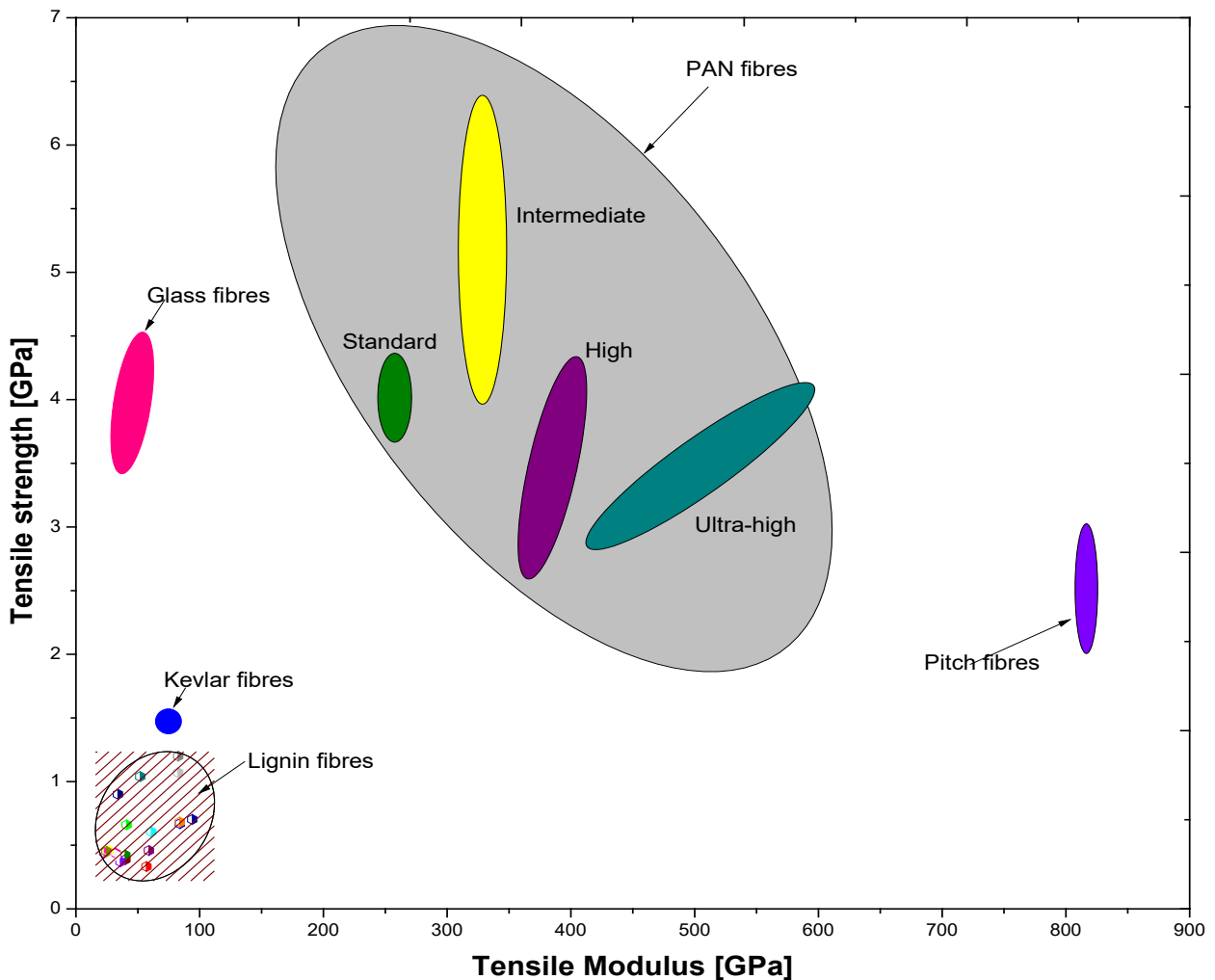


Figure 9.2: Mechanical performance map of carbon fibres from lignin in comparison to synthetic counterparts. Data for lignin carbon fibres are obtained from different studies on lignin carbon fibres [15–24]. Data for Pan, pitch, glass and Kevlar are obtained from Lin et al. [25].

Mechanical performance for lignin-based carbon fibres are illustrated in Figure 9.2. The tensile strength of lignin carbon fibres is only one-third of those of PAN based carbon fibres. The highest single filament tensile strength reported by Baker et al. [26] is 1.2 GPa and a tensile modulus of 82.7 GPa. This property is below that required for automotive applications (tensile strength: 1.72 GPa and tensile modulus: 172 GPa). Mechanical properties of lignin-based carbon fibres are dependent on several factors such as; source, extraction method, melt spinning, thermo-stabilization and carbonization variables. Tensile properties are also known to be dependent on the fibre diameter (Figure 9.3). Attempts have also been made to develop lignin nanofiber mats through electrospinning [25,27–34]. However, the mechanical performance are considerably lower than those of lignin carbon fibres (However, the mechanical performances of LCNFs mats (tensile strengths <100 MPa and tensile modulus <10 GPa) [35].

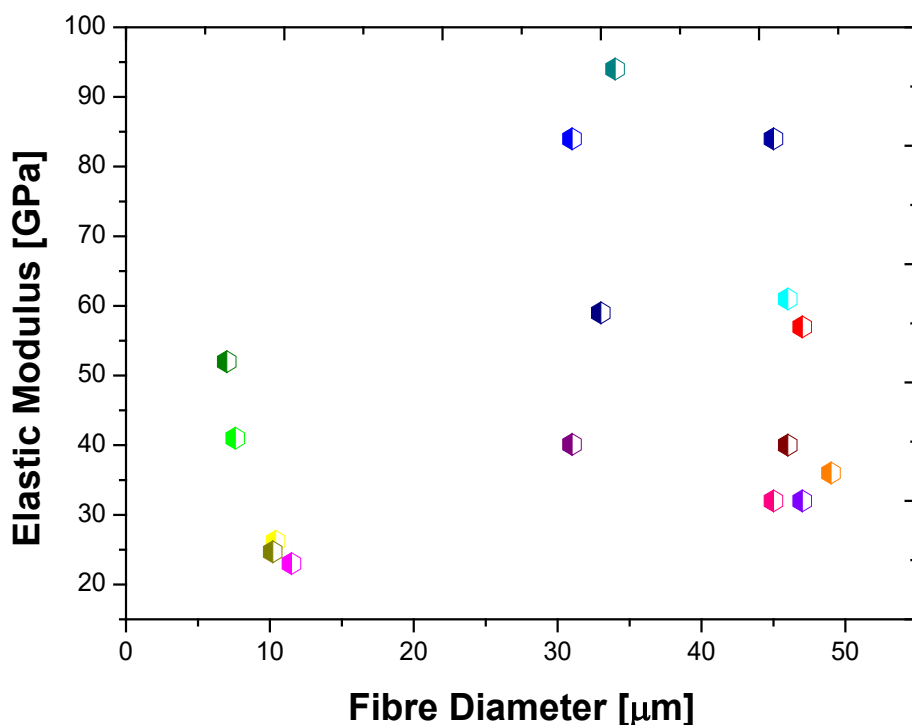


Figure 9.3: Variation of tensile modulus with fibre diameter. Data used in the figure are obtained from various publications

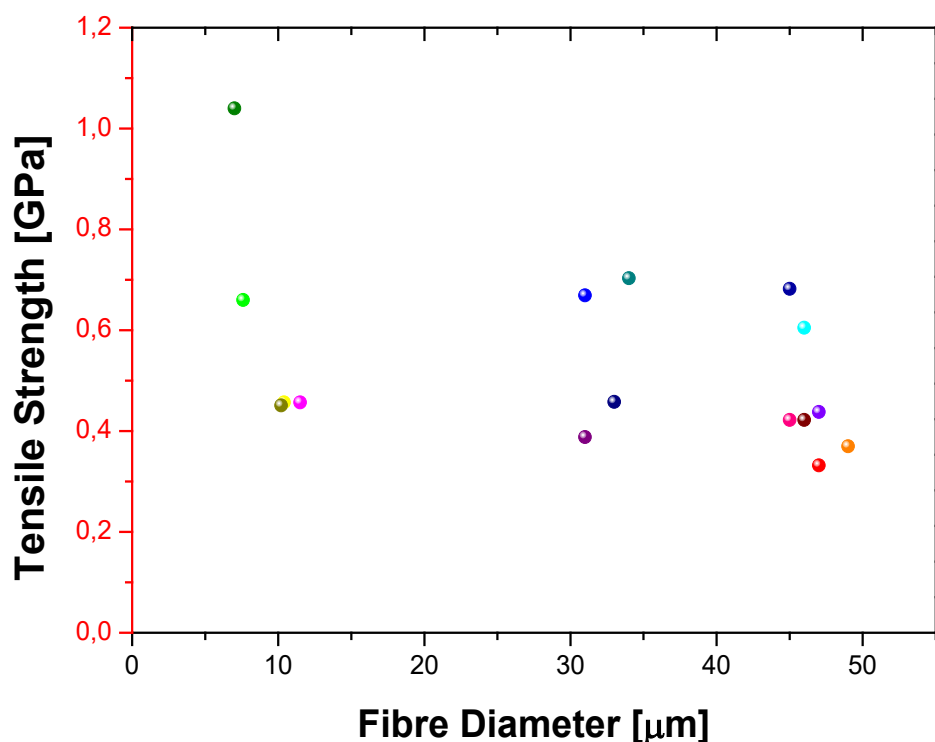


Figure 9.4: Variation of tensile strength with fibre diameter. Data used in the figure are obtained from various publications.

9.2.2 Applications of lignin carbon fibres

The reported mechanical properties of lignin carbon fibres do not meet applications such as automotive, wind turbine and aerospace applications. However, these fibres are found to be suitable for low level structural materials and other applications such as electrode applications, fuel cells, supercapacitors, electrodes for lithium ion batteries. Structurally, it has been noted that combining lignin with PAN, carbon fibres with mechanical performance suitable for internal parts, castings and tire frames can be fabricated [36].

Dallmeyer et al. [29] showed the lignin carbon fibres can be used as a precursor for flexible carbon electrode applications. Systematic control of the morphology of electrospun lignin samples to create interconnections during oxidation and carbonization led to the formation of fibre mat with improved tensile strength, ductility, and electrical conductivity suitable for carbon electrode applications. Rios et al. [6] reported the fabrication of electrodes for lithium ion batteries using lignin carbon fibres. The electrode composed of core shell silicon/SiO₂ islands embedded in the carbon fibres. The electrodes show capacities exceeding 700 mAhg⁻¹ with Coulombic efficiency of 99.5%. 3D electrically interconnected network and self-supporting material made from electrospun lignin fibres

have been fabricated for lithium ion battery anodes by Tenhaeff et al. [37]. The carbonized mat was found to cycle reversibly in conventional aprotic organic electrolytes with Coulombic efficiency over 99.9 %. Electrospun lignin carbon fibres have also been proposed as electrode materials for supercapacitor devices [5]. Interconnected and porous carbon fibre with submicron diameter, high surface area and conductivity was fabricated by electrospinning, stabilization and carbonization of Alcell lignin. The fabricated electrode shows power and energy densities of up to 61 kW/kg and 10 Wh/kg, respectively and can retain 100% and more than 90% of the initial power and energy densities, respectively, after 100 000 charge–discharge cycles at 5 A/g. Lia et al. [38] also produced free-standing and mechanically flexible electrospun lignin carbon fibre electrodes for high performance supercapacitors. In another study [32] the authors fabricated electro-catalyst for oxygen reduction reaction in alkaline fuel cells using electrospun lignin carbon fibres with mass resistivity higher than commercially sold catalyst. Wang et al. [39] also demonstrated lignin-derived nanocarbon material as effective energy storage material for lithium ion batteries. The electrospun interconnected nano-carbon fibres from lignin were found to outperform those of PAN in specific capacity and current density. Jin et al. [40] produced electrospun lignin carbon fibre webs containing different lignin–PAN ratios and carbonization temperatures as electrodes for sodium ion batteries. Ma et al. [41] coated lignin fibre mats with MnO₂ “nanowhiskers” as supercapacitors with gravimetric capacitance of 83.3 F g⁻¹, an energy density of 84.3 W h kg⁻¹, and a power density of 5.72 kW kg⁻¹. The use of lignin derived carbon fibres for supercapacitors has also been reported by Li et al. [42] and as high-capacity and high-stability lithium ion batteries by Chang et al. [43].

9.3 Lignin activated carbon

Activated carbons are porous carbon materials with very large surface area and very small pore volume. They possess interesting properties such as high thermal stability, high hydrophobic character, high chemical resistance and high adsorption capacity. They are used as absorbents in water and air purification, and gas separation, as catalysts or catalyst supports, energy conversion and storage and as electrodes in supercapacitors [44–54]. They are characterized by specific surface area, pore size distribution, and pore volume. Carbonized materials are transformed into activated carbon by activation using physical or chemical activation. A full description of the process of carbon activation can be seen in chapter 8. Primarily, coal, lignite, peat, wood, cocount shells and pitch are the traditional materials used to produce commercial activated carbon [55]. Numerous waste

resources have also been used to produce activated carbon including; hazelnut shell, rice husk, waste tires, fruit stones and municipal waste [56–60]. On the other hand, lignin contains a substantial amount of carbon and it is suitable for producing activated carbon. Lignin is a very attractive alternative to synthetic sourced activated carbon materials because it is cost effective, sustainable and renewable. Chemical and physical activation methods have been used to synthesize activated carbon materials from lignin [61–71]. Surface area and pore volume of activated carbon are measured experimentally by N₂ adsorption using adsorption isotherms. Surface area is usually measured using Brunauer-Emmett-Teller (BET) Model whereas pore volume is usually measured using Dubinin-Radushkevich (DR) model. A brief discussion of the various models and their significance is given in chapter 8. Other important properties of activated carbon include electrical conductivity, specific capacitance, power and energy density. These properties are dependent on the microporosity structure and pore distribution of the carbon material.

9.3.1 Properties of lignin activated carbon

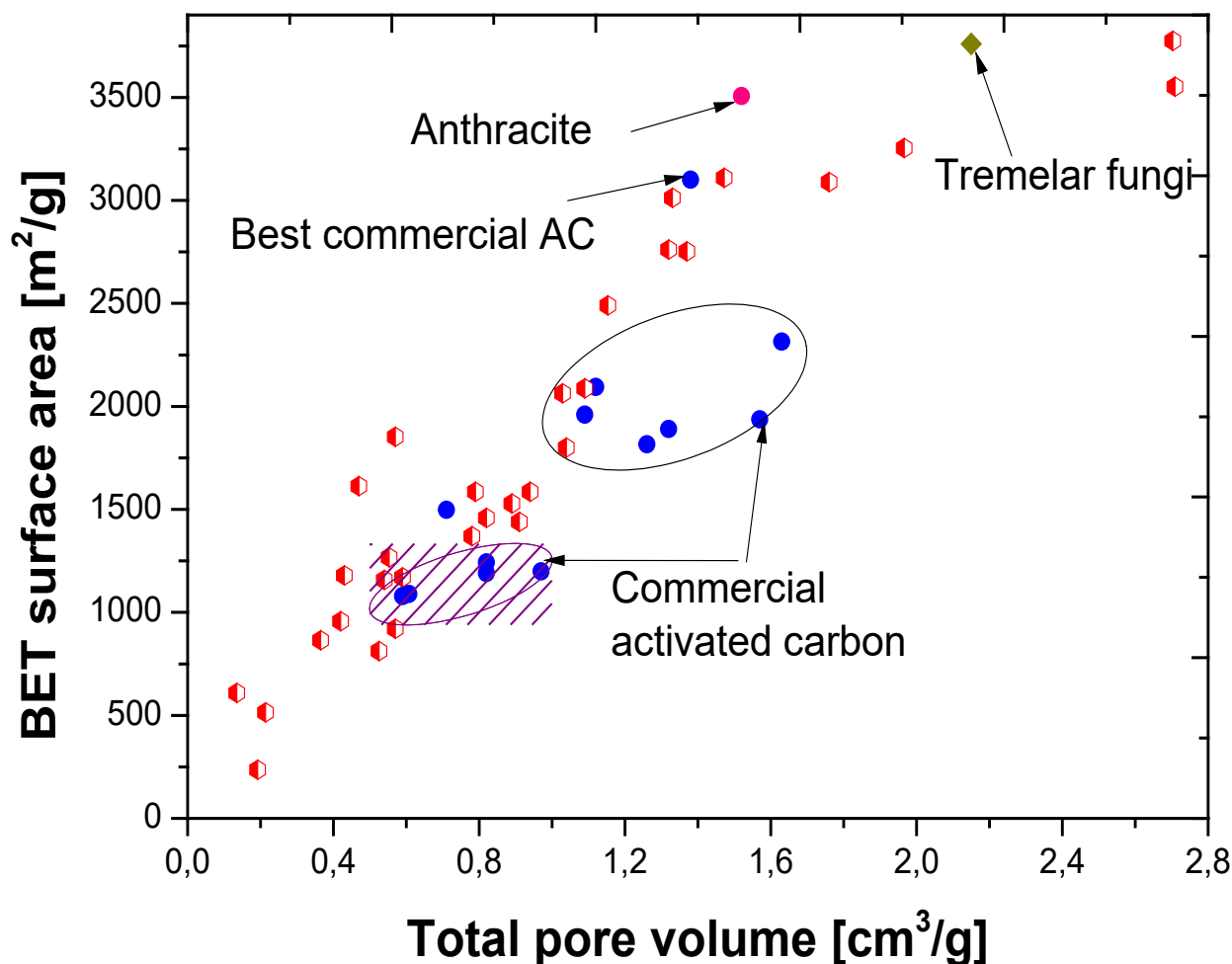


Figure 9.5: Performance of lignin based activated carbon. Lignin results are hexagonal and commercial ACs are circular. Data used in the figure are obtained from various publications [61,63–68,70–86].

A large surface area and pore volume are necessary qualities if activated carbon should be used as absorbents and electrical supercapacitors. A good supercapacitor should possess high specific capacitance, power and energy density which are dependent on electrical conductivity, surface area and microporosity [87]. Figure 9.5 shows the performance of activated carbon made from lignin from several studies using physical and chemical activation in terms of their surface area and pore volume. In most cases the surface area of lignin activated carbon are higher than those of commercial activated carbon from several sources including graphene and PAN. Lignin seems have the best performance as activated carbon based on surface area and pore volume. Lignin is very attractive as activated carbon because it is less expensive that carbon from sources such as SWNT, graphene and graphite oxide.

The use of activated carbon as a supercapacitor requires that the material possess a good specific capacitance. The optimal specific capacitance for commercial activated carbons ranged from 80 to 330 F/g for aqueous electrolytes and from 50 to 150 F/g for organic electrolytes [87]. Measurement of specific capacitance varies with scan rate (mV/s), electrolyte (organic and aqueous) and electrolyte concentration (M) as well as current density (A/g). These factors affect the values recorded for each sample making the comparison of results from different studies not possible. To show the comparative performance of lignin derived activated carbon in terms of specific capacitance against commercial and synthetic carbon materials, a series of results from different studies are presented in Table 9.1. It is obvious that lignin performs considerably in terms of specific capacitance compared to commercial activated carbon materials.

Table 9.1: Comparative electrochemical performance of lignin activated carbon

Precursor	Surface area (m ² /g)	Capacitance (F/g)	Electrolyte	Current density (A/g)	Ref.
Lignin	3500	413	1 M KOH	1.0	[88]
Lignin	1148	102	1 M KOH	0.2	[89]
Lignin	3775	287	1 M KOH	0.2	[85]
Lignin	1280	220	6 M KOH	1.0	[90]
Lignin	2265	336	6 M KOH	1.0	[91]
Lignin	855	281	1 M H ₂ SO ₄	0.5	[92]
Gelatin	3012	385	6 M KOH	0.05	[93]
Cotton	1085	207	1 M H ₂ SO ₄	1.0	[94]
Lignin	1100	226		1.0	[87]
Lignin	1400	344	1 M KOH	1.0	[34]
Anthracite	3012	204	1 LiClO ₄ /PC	0.04	[95]
Anthracite	3506	215	1 LiClO ₄ /PC	0.04	[95]
Bituminous coal	2105	167	1 LiClO ₄ /PC	0.04	[95]
Bituminous coal	2123	161	1 LiClO ₄ /PC	0.04	[95]
Maxsorb	3304	217	1 LiClO ₄ /PC	0.04	[95]
Anthracite	2647	220	1 LiClO ₄ /PC	0.04	[95]
PICA	1937	100	1.7M TEAMS/AN		[86]
PICA	2088	105	1.7M TEAMS/AN		[86]
PICA	1937	75	1M TEAM/PC		[86]
PICA	2088	90	1M TEAM/PC		[86]
Bituminous coal	2740	286	6 M KOH	0.1	[81]
Bituminous coal	2510	262	6 M KOH	0.1	[81]
Bituminous coal	3030	260	6 M KOH	0.1	[81]
Bituminous coal	2550	235	6 M KOH	0.1	[81]
Tremelar fungi	3760	71	6 M KOH	1	[78]
Lignin	1585	263	6 M KOH	0.04	[96]
Lignin	1886	231	EMB1F4	1	[97]
Lignin	1243	234	1 M H ₂ SO ₄	0.125	[98]
Lignin	2233	312	6 M KOH	1	[99]

9.3.2 Applications of lignin activated carbon

As shown in Table 9.1 lignin based activated carbon show very good specific capacitance which makes them useful as supercapacitors. A supercapacitor with energy density of 7.8 Wh/kg and power density of 47 kW/kg with over 92 % capacitance retention has been fabricated from lignin by Hu and Hseih [87]. In another study Liu et al. [92] supercapacitor with a charge density of 14.3 Wh/kg and power density of 2861 W/kg. Wang et al [91] also fabricated a symmetric supercapacitor using lignin. Another study also realized a supercapacitor with power density of 1897 W/kg and energy density of 5.8 W/kg. Lignin activated carbon has been applied to separate He from He-CH₄ mixture [71]. Zulamit et al. [98] also reported the fabrication of bio-xerogels with lignin activated carbon. Lignin activated carbon was also shown as a good absorbent for methylene blue [64]. Yu et al.

[99] also fabricated a supercapacitor with specific capacitance $14 \mu\text{Fcm}^{-1}$. Lignin activated carbon for effective absorption of phenol, 2,4,5-trichlorophenol and Cr (VI) [67]. Song et al. [100] fabricated lignin activated carbon as an absorbent for treating gaseous streams. Gustafsson et al. [101] fabricated Kraft lignin absorbent for effective sediment remediation.

9.4 Economic efficiency of lignin carbon fibres

9.4.1 Commercial viability of carbon fibres

Carbon Fibre Potential Market

The use of carbon fibres in structural applications enables the construction of extremely lightweight products without compromising safety. Carbon fibre composites possess high rigidity with the ability to absorb large amount of energy making them extremely damage tolerant. The unique combination of light weight and high strength of carbon fibre composites in contrast to metals makes them desirable in automotive, aerospace and marine applications. In addition, carbon fibre composites are corrosion resistant with design flexibility. The design flexibility coupled with high specific strength creates usefulness for them in wind energy, off-shore and compressed gas storage devices [102–105]. Because of the wide area of applications, carbon fibres have a large potential market. Figure 9.6 shows the estimated projection of the demand for carbon fibres between 2010 and 2022. The projection predicts an expected continuous rise in the demand for carbon fibres with an estimated average demand of 120.5 thousand tonnes in 2020. In 2017 carbon composites reported an annual carbon fibre demand of 70.5 thousand tonnes indicating a growth rate of 11 % over 2016 (63.5 thousand tonnes). Lignin carbon fibres are becoming necessary because of the need for the supply of cost effective, renewable and environmental friendly carbon fibres. Secondly, it is anticipated that with dwindling fossil minerals, alternative sources of carbon fibres are needed to sustain the growing demand.

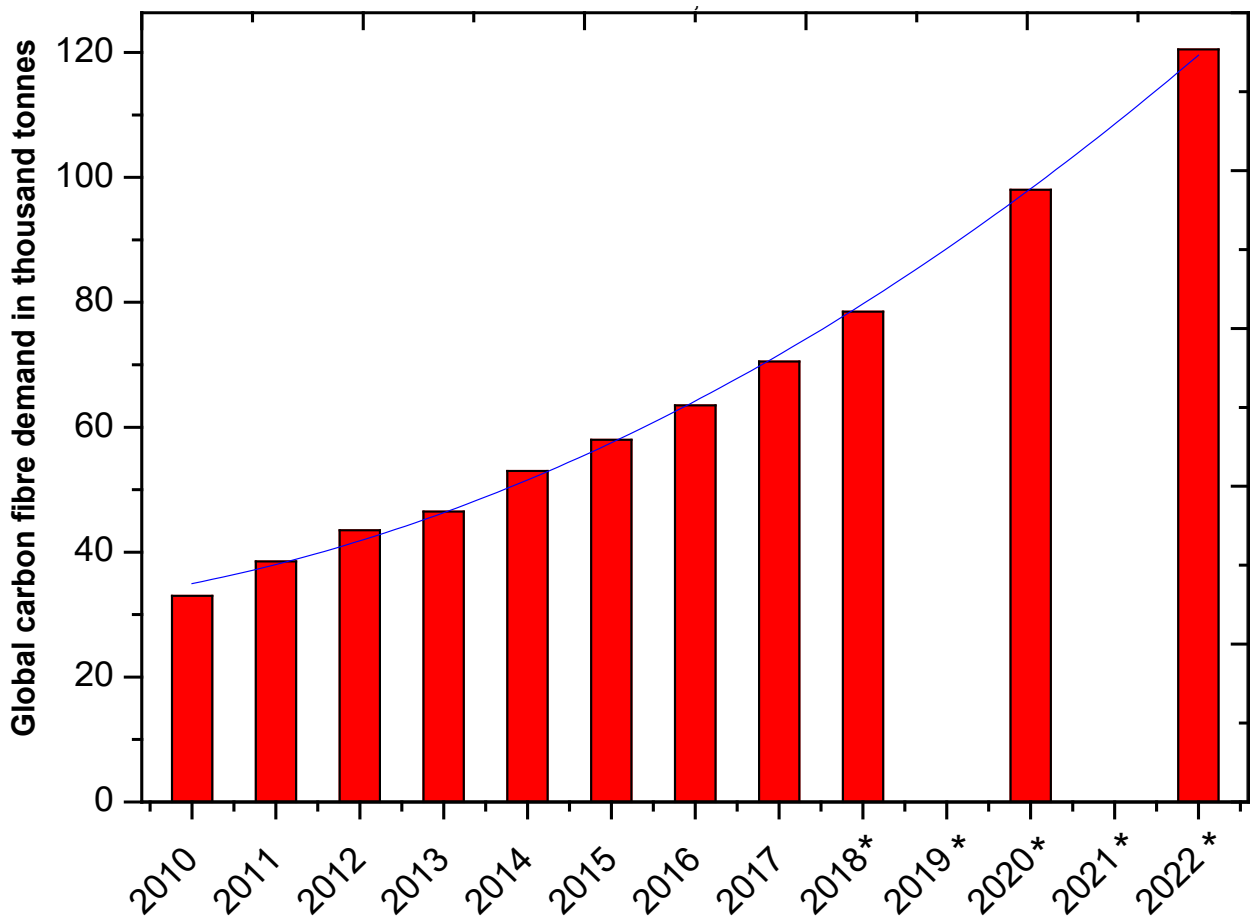


Figure 9.6: Global demand for carbon fibre in thousand tonnes 2010–2022. Adapted from 2017 Carbon Composites report. Data with * are projected values.

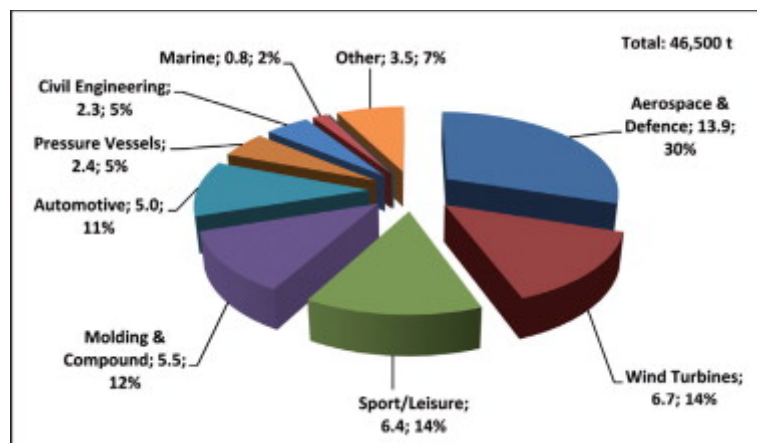


Figure 9.7: Global carbon fibre demand by application in thousand tonnes as at 2013. Reprinted with permission from Elsevier [104].

The demand for carbon fibre as at 2013 in terms by applications is given in Figure 9.7. The three fastest growing potential markets for lignin-based carbon fibres are automotive, wind and aviation. Lignin nanofibers also have a potential for electromagnetic shielding. In following section, the demands for carbon fibres in these application areas are presented [106].

Automotive

The automotive industry happens to be one of the key drivers of the carbon fibre market. The main driving force for the use of carbon fibres in the automotive industry is the need to improve fuel economy, reduction in CO₂ emission, lightweight construction, e-mobility, and pressurised containers for gas fuelled cars. For electric cars to be operational there is need for lightweight structural components [103]. The use of carbon fibres in the automotive sector grew from 5 % in 2012 to 11 % in 2014. An annual growth of 15 % was forecasted for automotive applications [106]. It was also predicted that the global carbon fibre market size in 2017 for the automotive industry will be about \$1,525 million based on the \$11 per kg estimate of ORNL [106]. BMW is also actively investigating the use of carbon fibres in several areas of automobiles and announced two million dollars (\$200) increase in investment at 2015.

Aerospace

One of the most important profile applications of high-modulus carbon fibres is the aerospace industry. Currently, carbon fibres have been applied in two new wide body aircrafts, Boeing 787 Dreamliner and Airbus A350 XWB with 50 % by weight carbon fibre composites. In Boeing 787 Dreamliner, 1500 aluminium sheets and 40000 fasteners was replaced with a one-piece carbon fibre composite fuselage. Carbon fibre composites are also used in aerospace wings, empennage and flight control surface on single aisle commercial aircraft [107]. It is estimated that carbon fibre usage in aircraft body will increase to about 9000 tonnes in 2020 [106]. SGL Group announced the introduction of carbon fibres with high Young's modulus suitable for pressure vessels, drive shafts and profiles in aerospace applications [108].

Wind energy

The switch from fossil-based energy sources to renewable sources has seen the development of wind turbines to the top of energy producing sources. It is anticipated that wind turbines with longer blades (>140 m) that can produce 20 MW of energy will be feasible in 2020. Carbon fibre is the only material suitable for constructing rotor blades with a length greater than 40 m. These wind turbines require a high proportion of carbon fibres in the supporting structures to guarantee stability and acceptable weight. This indicates that the need for carbon fibres in wind energy industry will grow significantly. Increase in the awareness of the viability of wind turbines in energy harvest will undoubtedly see many countries investing in wind energy which will result in increase in carbon fibre demand

[104]. However, the demand for carbon fibres in wind turbines was found to decrease drastically from 23 % in 2012 to 14 % in 2013. The wind energy market for carbon fibre is strongly dependent on the availability and value of carbon fibre. In 2013, 6700 tonnes of carbon fibres were consumed in the wind energy market. The decrease in demand between 2012 and 2013 is attributed to financial and technical difficulties [104].

Carbon Fibre Supply Chain

The global carbon fibre supply is best measured by the production capacity of the companies. This method of measurement is not very (100 %) realistic because the quoted capacities of these companies are more than likely not achievable for reasons of; increased downtime, reduced plant availability, increased discard etc. Moreover, the worldwide demand for carbon fibre production may not be completely quantified and may be higher than reported. Figure 9.8 shows the annual production from each of the firms for 2017. The total production capacity lies at 136.5 kilo tonnes/annum which is far higher than the demand value recorded in Figure 9.6. Aside the uncertainties surrounding the stated values, it is also possible that the carbon fibre supply is in excess for some applications and far less than the demand in others. Contrary to the forecast in Figure 9.8, Composites Forecasts and Consulting LLC's (Mesa, AZ, US) published a prediction in 2016 for overall carbon fibre demand and supply through 2020: The forecast showed that in 2010 demand for carbon fibres exceeded supply by over 1000 metric tonnes but in 2015, supply of carbon fibres will exceed demand by over 10000 metric tonnes [109]. However, their estimate shows that in 2020 the demand for carbon fibres will exceed supply by over 20000 metric tonnes. This is in line with carbon fibre supply and demand forecast chart reported by High Performance Composites [110] in 2010 (Figure 9.9). The figure shows that as from 2010, the demand for carbon fibres will stay ahead of supply. Table 9.2 compares estimated demand and supply of carbon fibres according to their applications as compiled by Waren [111] in 2010. In most applications the estimated demand range exceeds supply.

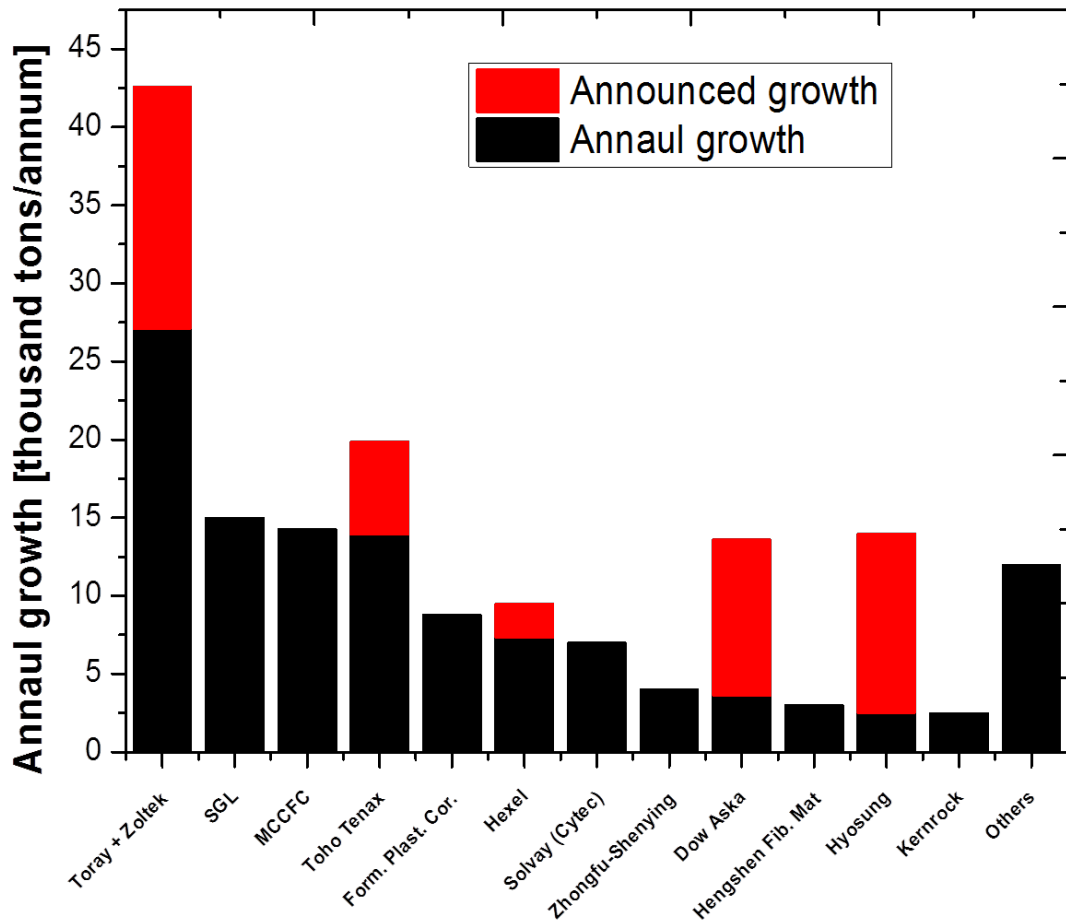


Figure 9.8: Theoretical annual carbon fibre production capacity by manufacturer as at 2017. Adapted from [112].

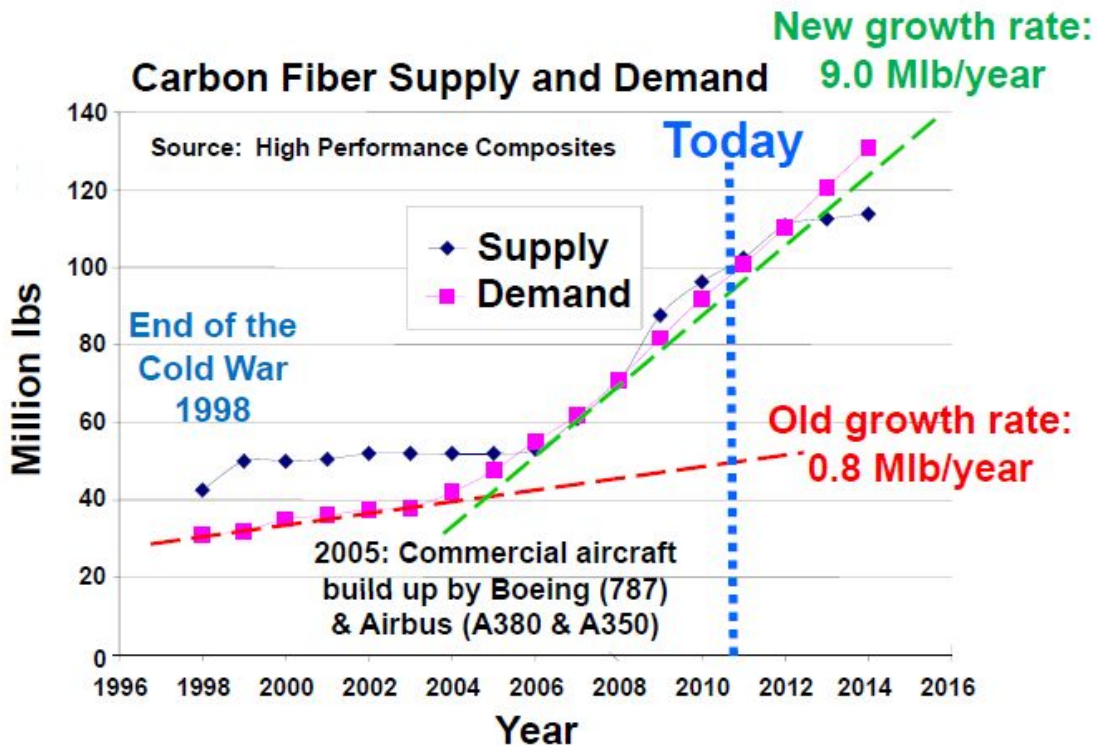


Figure 9.9: Carbon fibres supply, and demand forecast [110].

Table 9.2: Supply chain of carbon fibres according to applications [111]

Industry	Application areas	Market need (lbs/year)	Market supply (lbs/year)
Electrical Energy Storage	Li-Ion Batteries; Super-capacitors	10-50M	1-5M
Aerospace	Fairings; seat structures; luggage racks; galley equipment	10-100M	1-10M
Infrastructure	Retrofit and Repair of Aging Bridges and Columns; Pre-tension Cables; Pre-Manufactured Sections; Non-Corrosive Rebar	1-100B	1-10M
Electronics	Consumer Electronics	10-100M	1-10M
Non-Traditional Energy Applications	Structural members; Thermal management, Energy storage	10M-1B	1-10M
Automotive	Throughout Body and Chassis	> 1B	< 1M
Wind Energy	Blades and Turbine Components that must be mounted on top of the towers	100M -1B	1-10 M
Electrical Storage and Transmission	Low Mass, Zero CTE transmission cables; Flywheels for Energy Storage	10-100M	< 1M
Pressure Vessels	Hydrogen Storage, Natural Gas Storage	1-10B	< 1M
Oil & Gas	Pipes, Drill Shafts, Off-Shore Structures	10 -100M	< 1M
Defense	Ship Structures; Support Equipment; Tanks; Helicopters	10-100M	1-10M

9.4.2 Cost analysis of lignin carbon fibres

The key processing steps in the production of carbon fibres from lignin includes; extraction, purification, melts processing, stabilization, carbonization, in some cases carbonization and finally surface treatment (Figure 9.10). Generalizing cost analysis for the processing of lignin carbon fibres will be difficult as the various stages involve different processing methods and equipment. For example, extraction of lignin can be done in several ways including Kraft extraction, sulphite, Organosolv etc. These processes involve the use of different chemicals and equipment which make the cost different from each other. Baker [6] reported that Kraft lignin extraction cost 0.44 \$/kg but that of Organosolv is 1.14 \$/kg. Purification of Kraft lignin also cost 1.14 \$/kg but Organosolv lignin does not

require extra purification. This shows that cost analysis of lignin should be initially based on the processing route. The design strategy in this case should consider the difference in the extraction method, processing route and parameters.

In standard production cost analysis, key inputs, processing steps, outputs, equipment cost, overhead, capital cost, probable yield and rate limiting steps are usually considered. In the case of lignin carbon fibres, the key input is the lignin precursor and the processing steps are shown in Figure 9.10. Details of each step have been discussed in various chapters of this book. The outputs are different grades of carbon fibres. The output quality is usually measured in terms of tensile strength and elastic modulus.

The equipment cost, overhead and capital costs are analysed for each of the processing step. Industrially, the production of lignin is performed in continuous operation in three sections; (A) pulping, (B) precipitation and purification and, (C) fibre processing. Pulping is a very capital intensive industry which is usually aimed at producing paper. The waste product of this paper industry is the black liquor which is the starting raw material for the production of lignin. Approximately seven (7) tonnes of black liquor are produced in the manufacture of one (1) tonne of pulp. The liquor contains between 35 – 45 % lignin [113]. In lignin carbon fibre cost estimation, the equipment and capital cost of pulping is not usually considered.

Cost analysis of carbon fibre production begins with precipitation and purification processes. Precipitation and purification involve the extraction of lignin from the black liquor produced by the pulping industry and further removal of impurities to obtain solid lignin of considerable purity. A few commercial processes exist for the precipitation and purification of lignin from the black liquor including; LignoBoost®, LignoForce®, Biolignin®, BioChoise® and Lignol® [12]. The major hurdle in the production of lignin has been the implementation of these processes. The pulping industries mostly resist the incorporation of these processes because they are capital intensive and mostly, the industries are afraid of the risk involve in incipient technology. The most widely adopted process is the LignoBoost® process which is applied to Kraft lignin. The equipment requirement for the LignoBoost process is roughly 25×20×14 m³ in size and is capable of producing 175 - 295 kg of lignin per tonne of black liquor. Operating at a capacity of 50,000 tonnes of lignin annually requires a total investment cost in the range of \$12 – 18 million and an operational cost in the range of \$60 – 110 per tonne of dry lignin. The process consumes

150 – 320 kg/tonne of lignin and acid of 120 – 255 kg/ tonne of lignin [114]. LignoForce® has also been commercialized with a capacity of 30 – 50 tonnes of lignin per day. The estimated price of lignin from LignoForce® is \$1.1 per kg. Lignin fibre processing involves the processes from melt processing to packaging. The process differs between companies and are custom tailored to of each production making them expensive. The capital and equipment cost is the range of \$ 25 – 100 million depending on the output and annual capacity [115].

Other important aspects of cost analysis of lignin carbon fibres are the yield, scrap rate, rate limiting steps and the economic scale. The lignin carbon fibre yield is measured as the total mass of lignin obtained after carbonization of the lignin fibre. There have been reports of increase in the yield of lignin up to 50 – 60 %. The scrap rate is the percentage of knockdown after production. It is dependent on the production efficiency. The efficiency of lignin fibre production can be equated to that of PAN production since the follow a similar process. Report shows that efficiency of PAN production is over 60 % and may approach 70 % in 2020 [107]. The rate limiting step in the production of lignin carbon fibres is the oxidation step. The efficiency of the oxidation furnace is a critical determinant of the overall production process. These factors are important in the cost analysis of lignin carbon fibres and should be taken into consideration. Generally, the cost analysis involves the development of models using the above factors. At present, a few models have been developed to analyse the production cost of lignin carbon fibres. In the following section three of these models are presented.

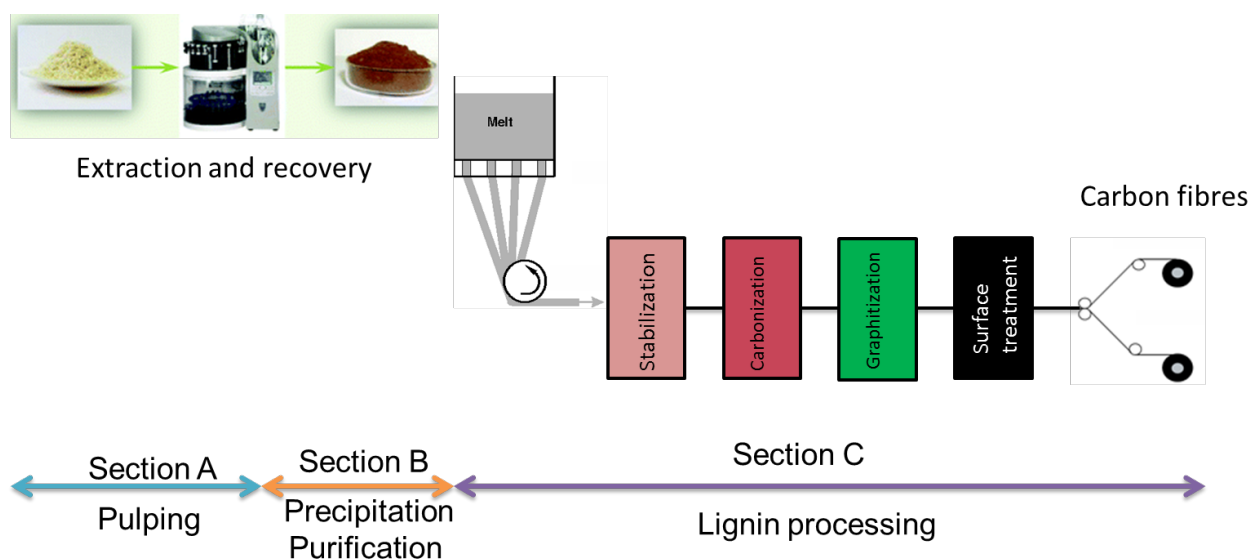


Figure 9.10: Key processing steps in the production of carbon fibres from lignin

Kline Economic model

In 2007 Kline and co. conducted a cost study funded by the Automotive Composites Consortium (ACC), to evaluate the effectiveness of carbon fibre research and determine future research directions [116]. Results of the study included a baseline cost model for the manufacturing cost of carbon fibres. The baseline model indicates that precursor cost is the rate determining cost (accounts for over 50 % of the total production cost) for the overall production of carbon fibres. For fossil based precursors, the precursor cost fluctuates with the cost of crude oil. To eliminate the uncertainties, alternative precursor sources were suggested including lignin. The model further examined the use of lignin as precursors using conventional. Hardwood and softwood lignin had the most substantial prospect for cost savings but also possess a higher degree of scientific uncertainty (Figure 9.11). Considering alternative processing methods, the model was extended to arrive at substantial cost savings. The model was formulated based on the following baselines and assumptions:

Baseline spinning speed of 600 m/min

Absence of purification step

Stabilization step is based on PAN stabilization scheme

Maximum carbon yield of 35 %

The model proposed that when all the alternative technologies (application of microwave assisted plasma technology, advanced stabilization and advanced stabilization) are utilized the cost of production will be reduced (Figure 9.12). Recent study has shown that fibre spinning speed can be increased to almost 3 – 5 times the Kline spinning speed baseline [117,118]. On the other hand, stabilization time has been reduced to matter of minutes against and it may be possible to remove eliminate the stabilization time completely [20,119–121]. In addition, some studies realize yield higher than 55 % using appropriate lignin chemistry [24,122–124]. The Kline cost models are fairly rigorous but they are also conservative. They are generally useful for comparison and trending: selection of most promising research, identification of cost sensitivity, and establishment of scaling targets [125]. Using the Kline cost model Baker presented an estimate of \$3.71/lb [13] for lignin carbon fibres and \$2.85/lb [110] for nanoporous carbon fibre for electrical energy storage and applications as an adsorbent. The cost breakdown for these model applications are shown in Figure 9.13.

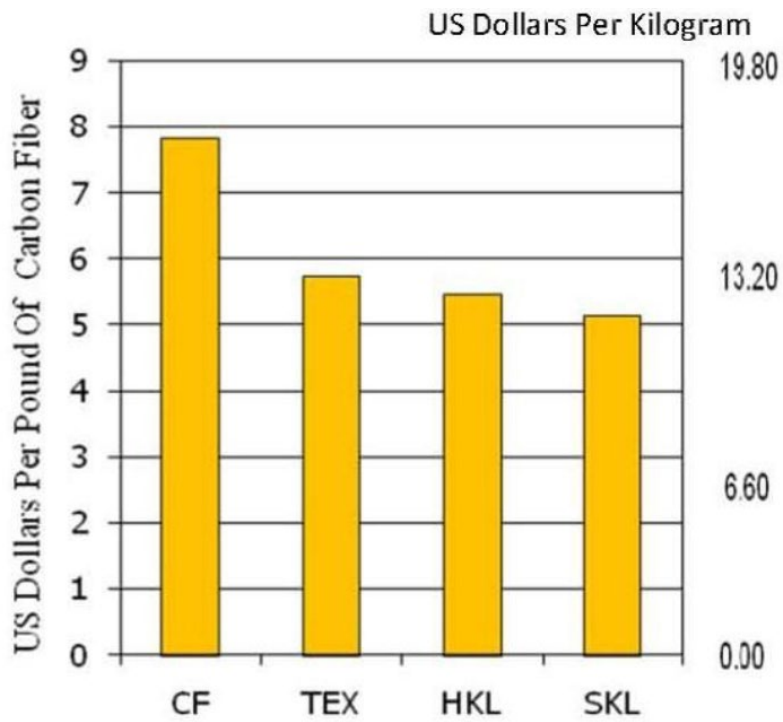


Figure 9.11: Carbon Fibre Costs Using Alternative Precursors and Conventional Processing [116].

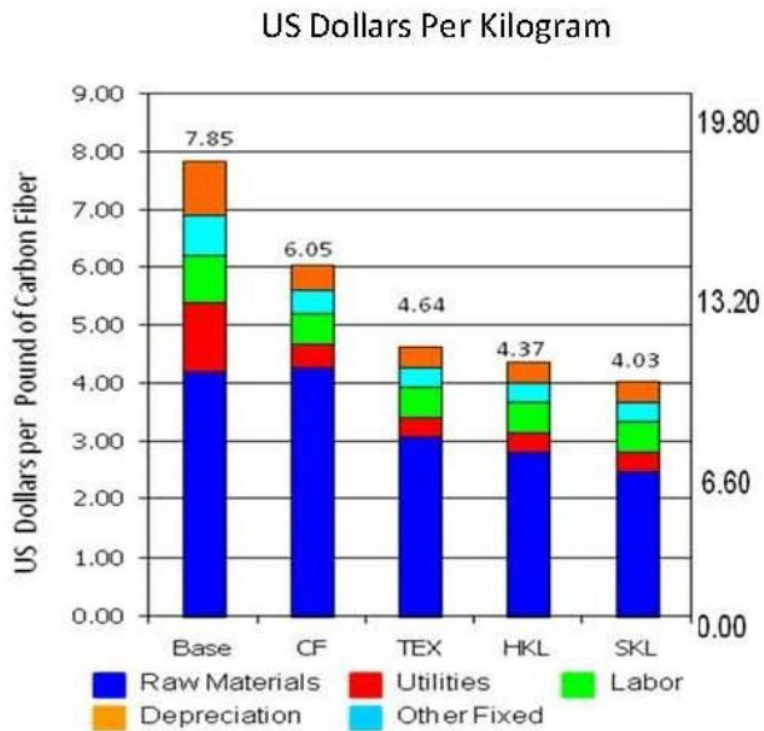


Figure 9.12: Carbon Fibre Costs using alternative precursors and alternative processing [116].

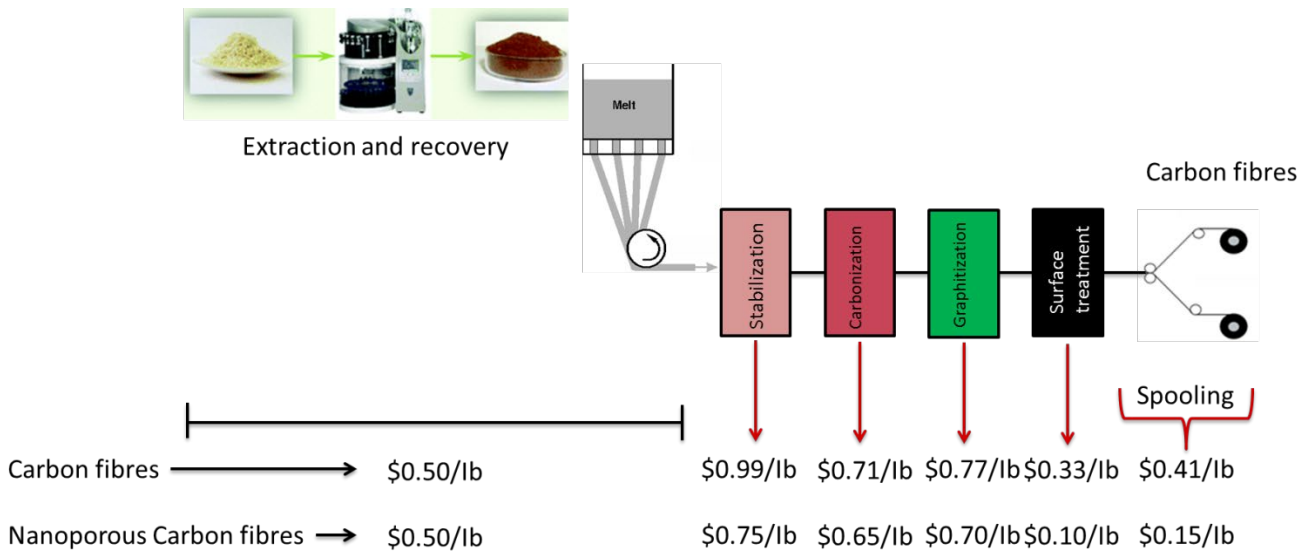


Figure 9.13: Cost breakdown for application of Kline model to carbon fibres and nanoporous carbon fibres.

ORNL model

A model for estimation of production cost of lignin fibres produced by melt blowing to form fibre mats and further processing using conventional stabilization and carbonization has been developed by ORNL [126]. The model accounted for energy usage, labour, capital and material requirements. The model is based on the following assumptions:

Lignin purchase price = \$0.25/lb

No purification is required before melt processing

Area density = 1500 g/m²

The web is not direct fed between spinning and heat treatment

Not tension is applied during carbonization

Stabilization time = 2 hours

Yield after heat treatment = 45 %

The model estimated a total production cost of \$4.22/lb (Figure 9.14).

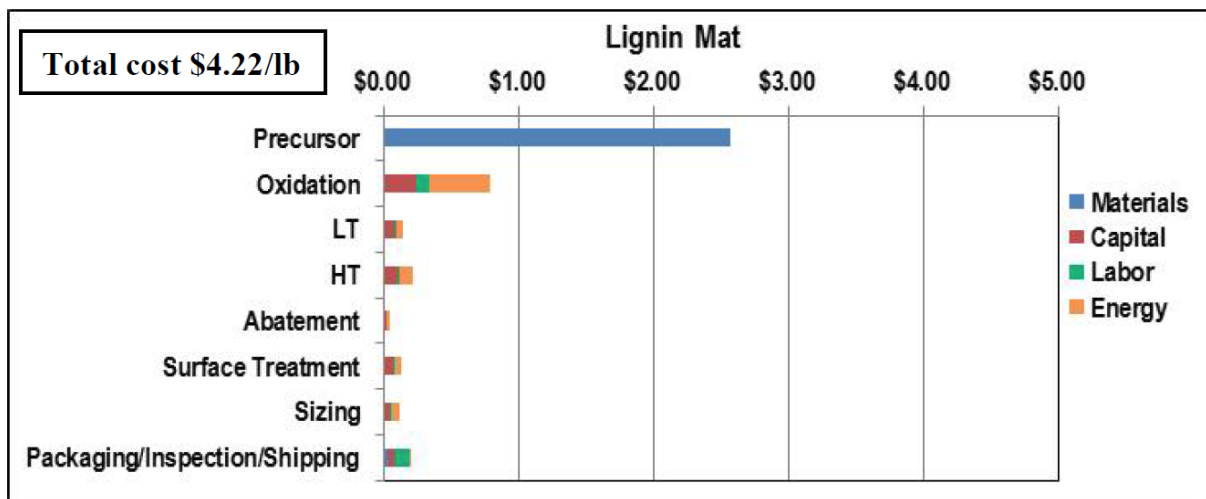


Figure 9.14: Estimated production cost of lignin carbon fibre web [126].

A critical assumption of the model is the stabilization time. The model used two hours based on laboratory experiment schedule, but this is not practical in the pilot scale where the stabilization time is almost 100 hours. However, it has been shown that with scalable treatment to replace the conventional vacuum baking, a stabilization time of 10 hours can be achieved. To account for the realistic stabilization time, a simple rule of thumb was applied to analyse the impact of changes in stabilization time on the overall cost. Approximating the unit conversion cost by equation 9.1 and using a scaling factor of 0.7, the change in cost with increase in stabilization time was deduced as shown in Figure 9.15. The analysis shows that with 10 hours of stabilization, a total production cost below \$5/lb can be obtained. Apart from stabilization time, another critical assumption in the model is elimination of purification cost. This restricts the model to certain precursors such as Organosolv lignin. Putting the yield at 45 % is a reasonable assumption, but as noted earlier some studies have achieved yield as high as 55 %. The model is only applicable to carbon fibre webs, not single fibres.

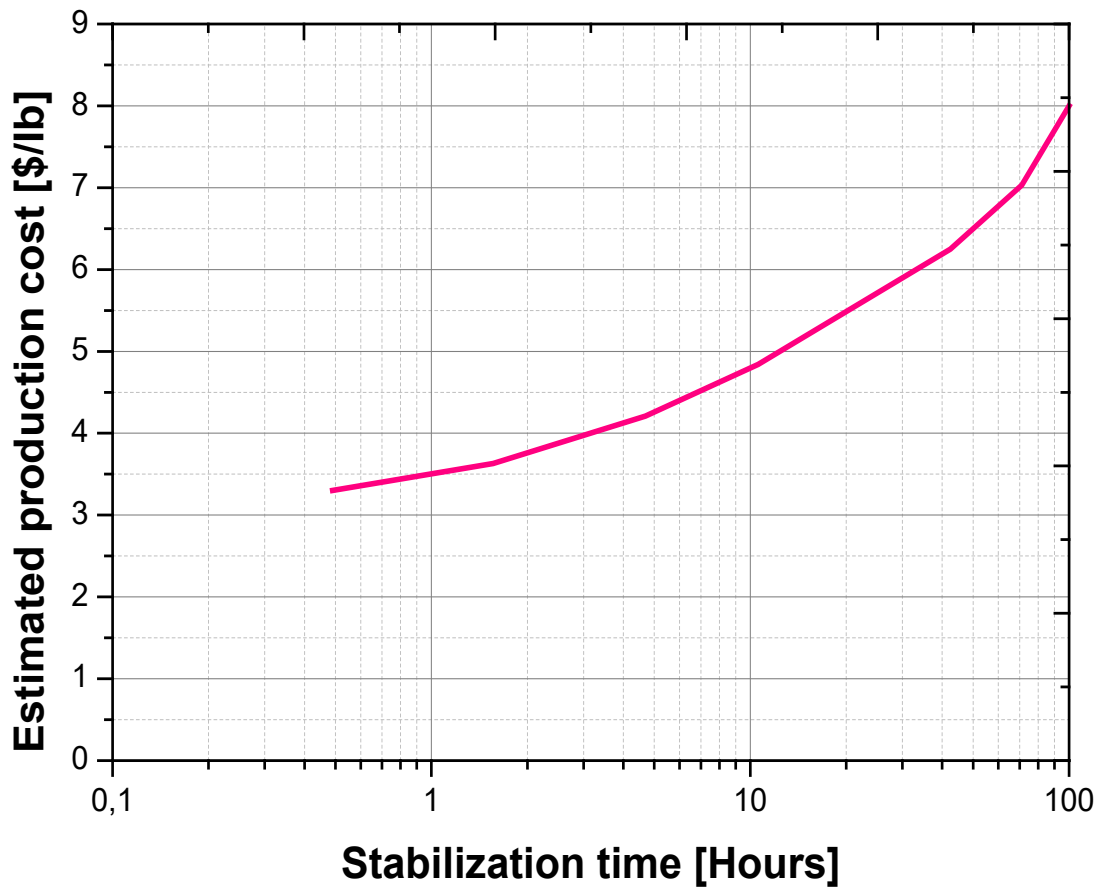


Figure 9.15: Estimated correlation of production cost with stabilization time [126].

$$\text{Unit Conversion Cost (\$/lb)} = C_r X^{n-1} \quad 9.1$$

where: C_r is the unit conversion cost at reference scale, X is the throughput increase factor, n is the scaling exponent.

GrafTech model

The GrafTech model was developed based on data from Harper International and ORNL [116,127–130]. The model assumes a higher purchase cost than the ORNL model. The model also takes into consideration the effect of lignin precursor cost, stabilization time, and yield after carbonization on the total cost of production. The model was developed with \$5.00/lb total production cost target and assumes the following:

Lignin purchase price = \$0.50/lb.

Lignin modification cost = \$0.20/lb.

Lignin melt blowing cost = \$0.88/lb.

Stabilization time = 2 hours

Yield after carbonization = 45%

Emissions abatement cost = \$0.04/lb.

Packaging cost = \$0.25/lb.

The model ignores the cost of surface treatment. An important aspect of the model is the ability to show the combination of variables that will meet a certain cost target.

The model showed that lignin precursor cost, stabilization time, yield after carbonization has the largest effects on total cost of production (Figure 9.16). A sensitivity plot (Figure 9.17) using the model highlights the magnitude of these effects on the estimated production cost. The analysis show that low stabilization time, high carbonization yield and low precursor cost are needed to achieve the target goal. Fibre yield after carbonization shows the largest relative effect followed by precursor cost and stabilization time. Correlating production cost, stabilization time and precursor cost (Figure 9.18) allows the determination of allowable leverage in cost and time to achieve a particular goal. For example, it is apparent from Figure 9.17 that additional \$0.25/lb of precursor cost can be afforded for every 2 hours reduction in stabilization time when the fibre yield is kept at 45 %. This means that if the stabilization time is reduced, additional processes like modifications and treatments can be introduced without raising the final cost of the production. The model is based on a 45 % yield but some studies have shown that yield as high as 55 % can be obtained [24,122–124]. The model does not account for surface treatment and sizing of the fibres. Figure 9.19 shows the breakdown of the cost for each key element in the model using four lignin samples.

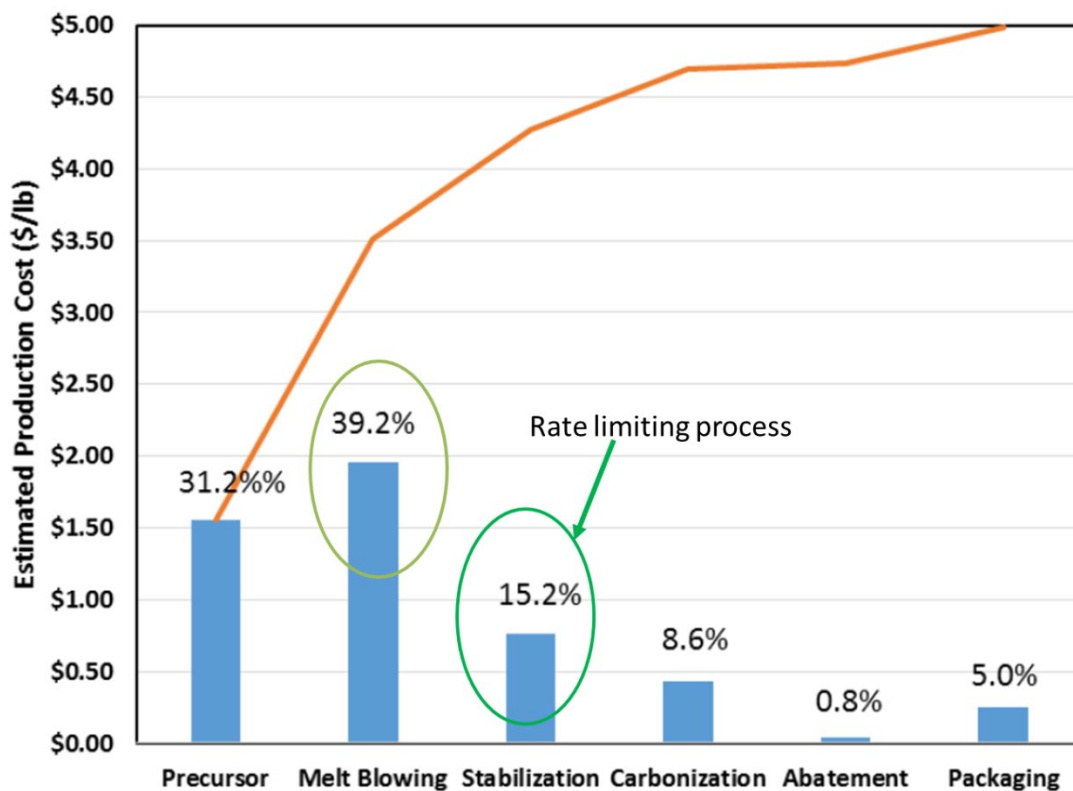


Figure 9.16: Contribution of processing steps to the total production cost [4].

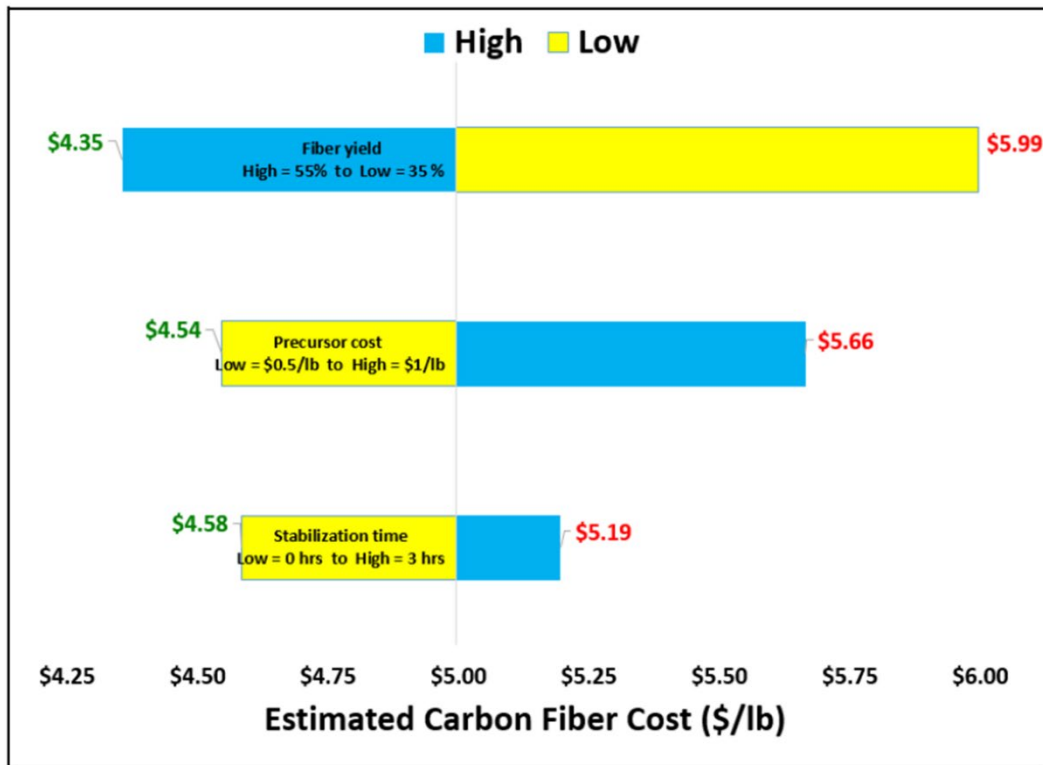


Figure 9.17: Sensitivity analysis [4].

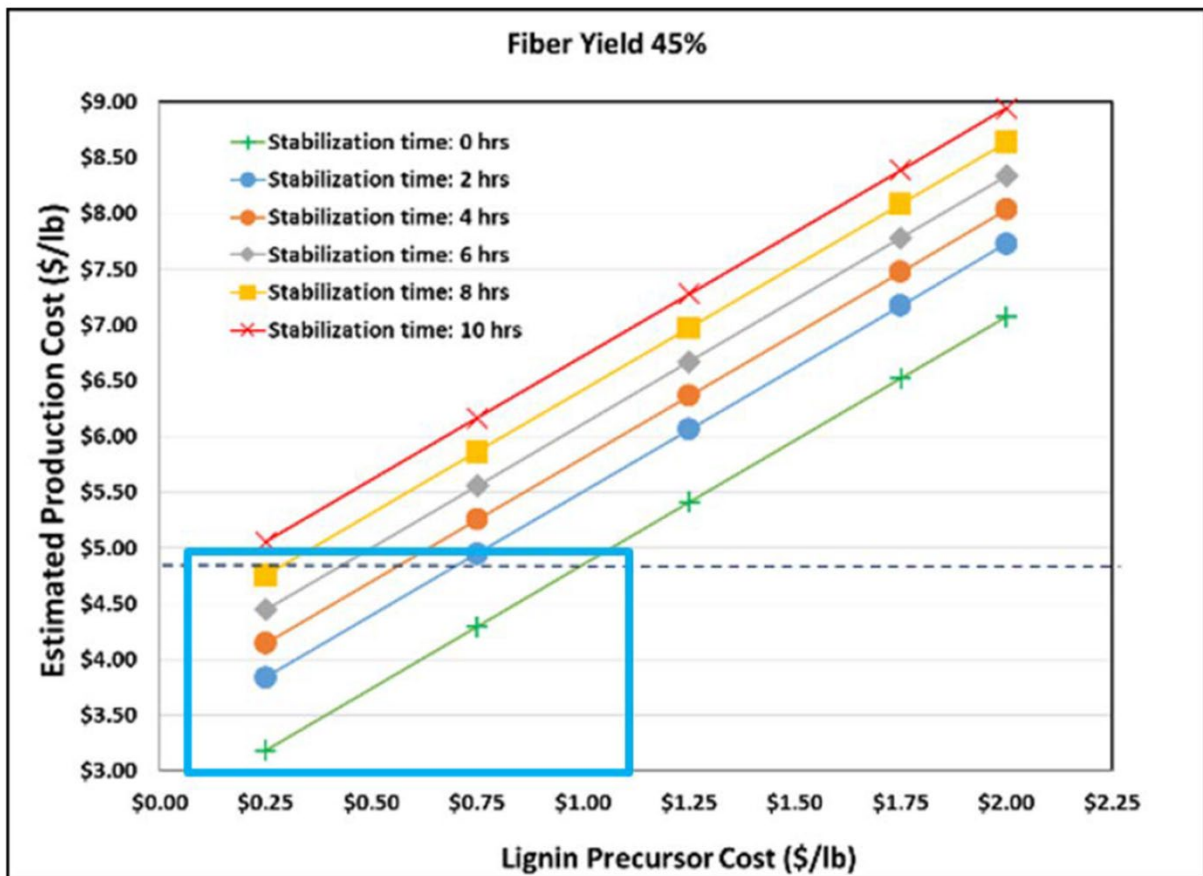
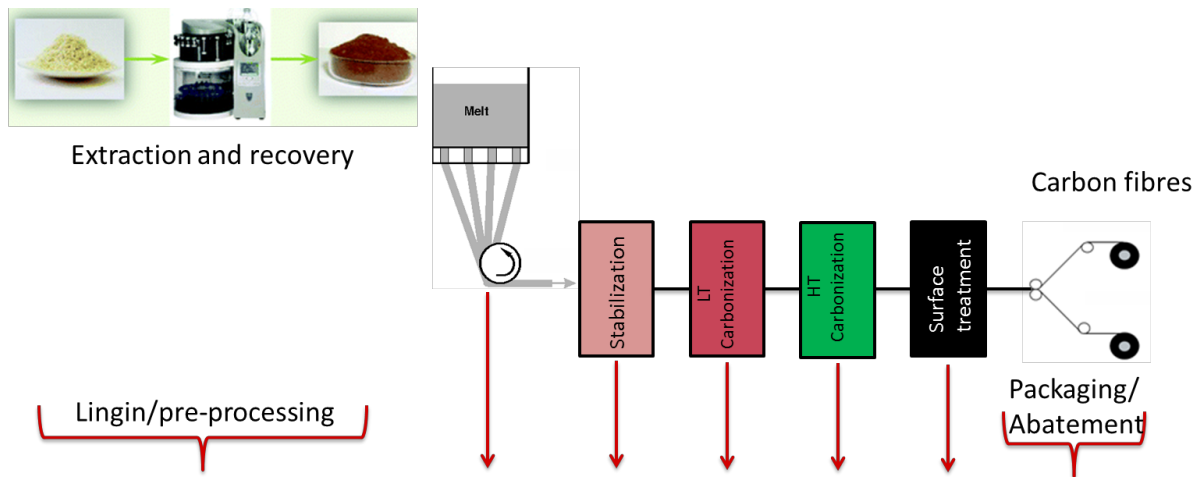


Figure 9.18: Predicted effect from cost model showing influence of stabilization time [4].



HW ORP (44 %)	\$2.43	\$0.88	\$0.96/180 min	\$0.17	\$0.26	--	\$0.29
Indulin AT (41%)	\$2.76	\$0.88	\$0.65/87 min	\$0.17	\$0.26	--	\$0.29
PB-100 (42%)	\$2,67	\$0.88	\$0.72/110 min	\$0.17	\$0.26	--	\$0.29
DD (44%)	\$2,48	\$0.88	\$0.86/150 min	\$0.17	\$0.26	--	\$0.29

Figure 9.19: Breakdown of model cost. Numbers in parenthesis in column 1 represent the final yield and the times of stabilization are shown alongside the cost in column 4.

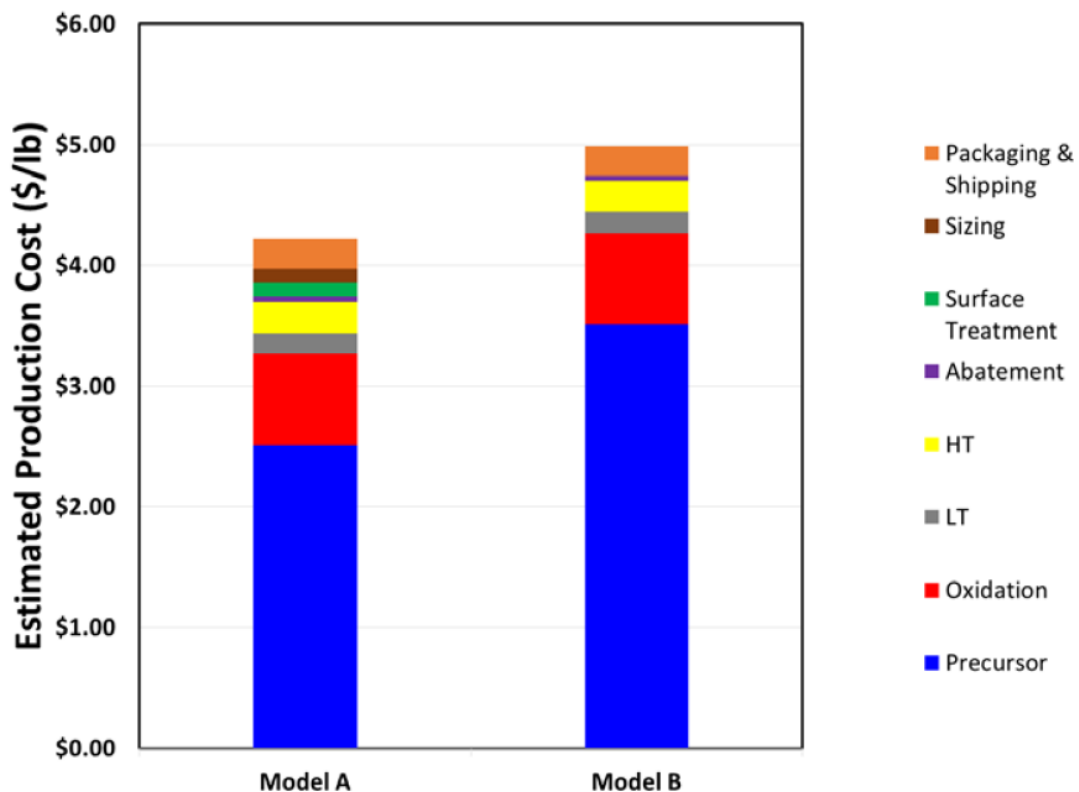


Figure 9.20: Comparison of two lignin cost models [4]. Model A is from ORNL model and Model B is for GrafTech [4].

Figure 9.20 compares the cost estimate for ORNL and GrafTech models. The major difference between the two models is the precursor cost which is higher for GrafTech. Moreover, surface treatment and sizing was not accounted for in the GrafTech model.

9.4.3 Environmental impact

To examine the environmental impact of producing lignin carbon fibres, it is important to consider the energy requirement, emissions and cost of emission management. Emissions which are considered of environmental impacts are CO₂ and HCN. Figure 9.21 shows the various stages in the production of lignin carbon fibres illustrating the various forms of environmental impacts. For most researchers, the extraction process of lignin belongs to the pulping industry. The energy requirement, emissions, chemical and water usage are appropriated to the pulping industry and are not usually considered during the assessment of lignin carbon fibre production route. Emissions in the lignin production process include; CO₂ and HCN emissions. These emissions are predominant in the melt processing, stabilization and carbonization stages. Lignin based precursors emits less volatile organic compounds and greenhouse gases during the process. This results in less energy consumption. The oxidation stage is the rate limiting step in terms of energy consumption and gaseous emissions. The energy consumption is heavily dependent on the efficiency of the oxidation process.

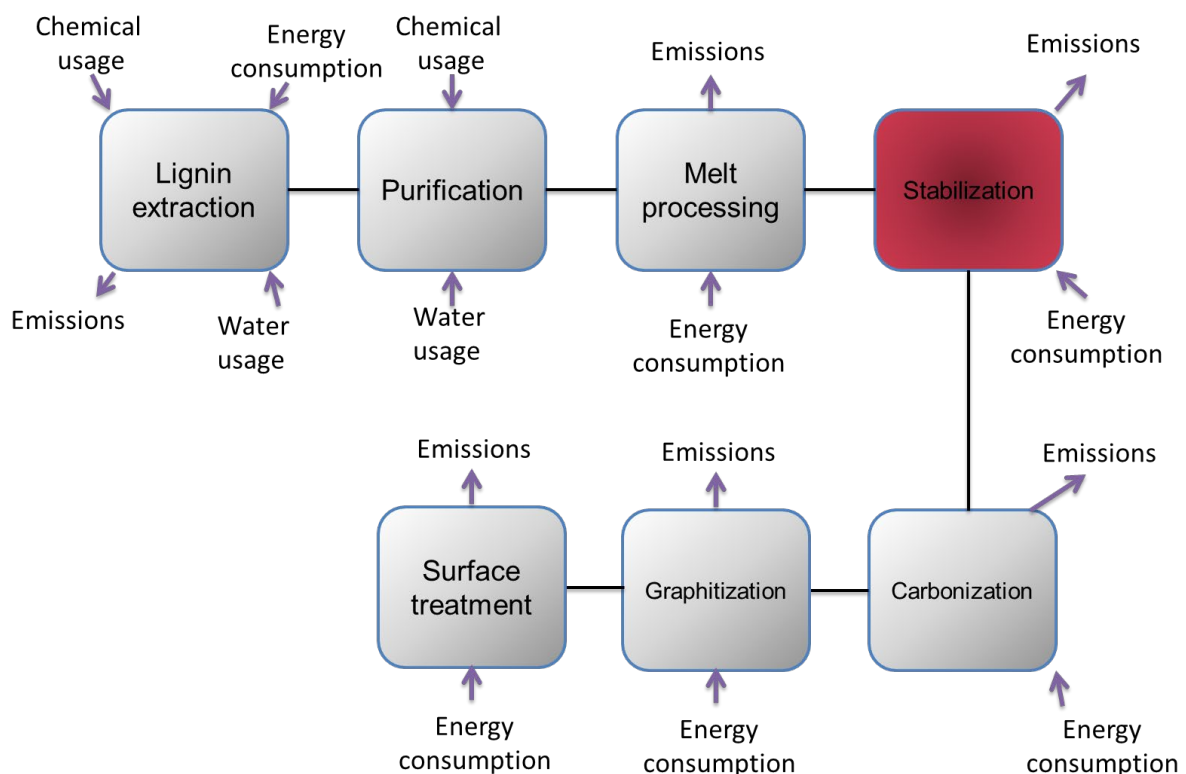


Figure 9.21: Environment impact factors in the production of lignin carbon fibres

A comparative analysis of CO₂ and HCN emissions between lignin and PAN processing is shown in Table 9.3 [115]. Lignin precursors show significant cost savings over conventional PAN precursors. If the cost of damage from an extra tonne of CO₂ to be \$37

per tonne, it can be deduced that lignin carbon fibre can save \$260 per tonne from CO₂ environmental impact compared to PAN fibres.

Table 9.3: CO₂ and HCN emission, and energy consumption of lignin and PAN fibre precursors [115]. Energy is calculated based on \$10 per 1GJ of energy, CO₂ cost is estimated at \$10 per tonne and HCN cost is estimated at \$11/kg.

	CO ₂ per kg of material	HCN per kg of material	Energy usage-precursor production/kg	Energy usage-final conversion/kg	Total
PAN	31 kg	12 kg	245 MJ	495 MJ	704 MJ
Cost	\$0.31	\$0.13	\$2.45	\$4.59	\$7.04
Lignin	24.2 kg	0	210 MJ	400 MJ	670 MJ
Cost	\$0.24	\$0	\$2.10	\$4.00	\$6.07
Savings	\$0.07	\$0.13	\$0.35	\$0.59	\$0.97

9.4.4 Economic risk factors

Basic problems facing the implementation of lignin as a precursor for the fabrication of carbon fibres are the risk factors involved in the production and application of the fibres.

Production of high purity lignin

Lignin purity is one of the major factors affecting the properties and cost of lignin fibre precursors. Lignin exists alongside hemicellulose, pectin, wax, cellulose and other materials in the bulk biomass making contain a certain level of impurities [142]. These impurities include carbohydrates, hemicellulose, sulphur, proteins, particulates, ash, inorganic salts, extractives, lignin-derived phenolics, metal-containing salts and water [143]. Some of these impurities affect melt processing of lignin in several ways [144–151]. Moreover, most processes solubilize lignin into high and low molecular weight fractions making it necessary to separate them before further processing as the difference in molecular weight is known to affect melt processing. Research has shown that impurities can lead to higher glass transition temperature of lignin. Removing these impurities involve the use of chemical and thermal methods and in some cases involve expensive instrumentation such as the use nano-filters. Most of the processes for lignin purification are purely in the experimental stages and have not been transferred to the industries. On the other hand, the industries are very conservative concerning the introduction of new processes which have not been proven.

Development of new processes

Although processing of lignin precursors to carbon fibres is to some extent similar (Figure 9.22) to conventional precursors such as PAN, it is still difficult to adapt existing processes to lignin carbon fibres processing. This creates the necessity of developing new processes. For example, it has been noted that micro-wave assisted plasma carbonization, UV assisted stabilization, etc. are necessary, if the properties of lignin carbon fibres must be improved [20,111]. These are novel processes that must be adapted into existing production lines. The adaptation is not only capital intensive but involve uncertainties that most industries will not want to commit investment.

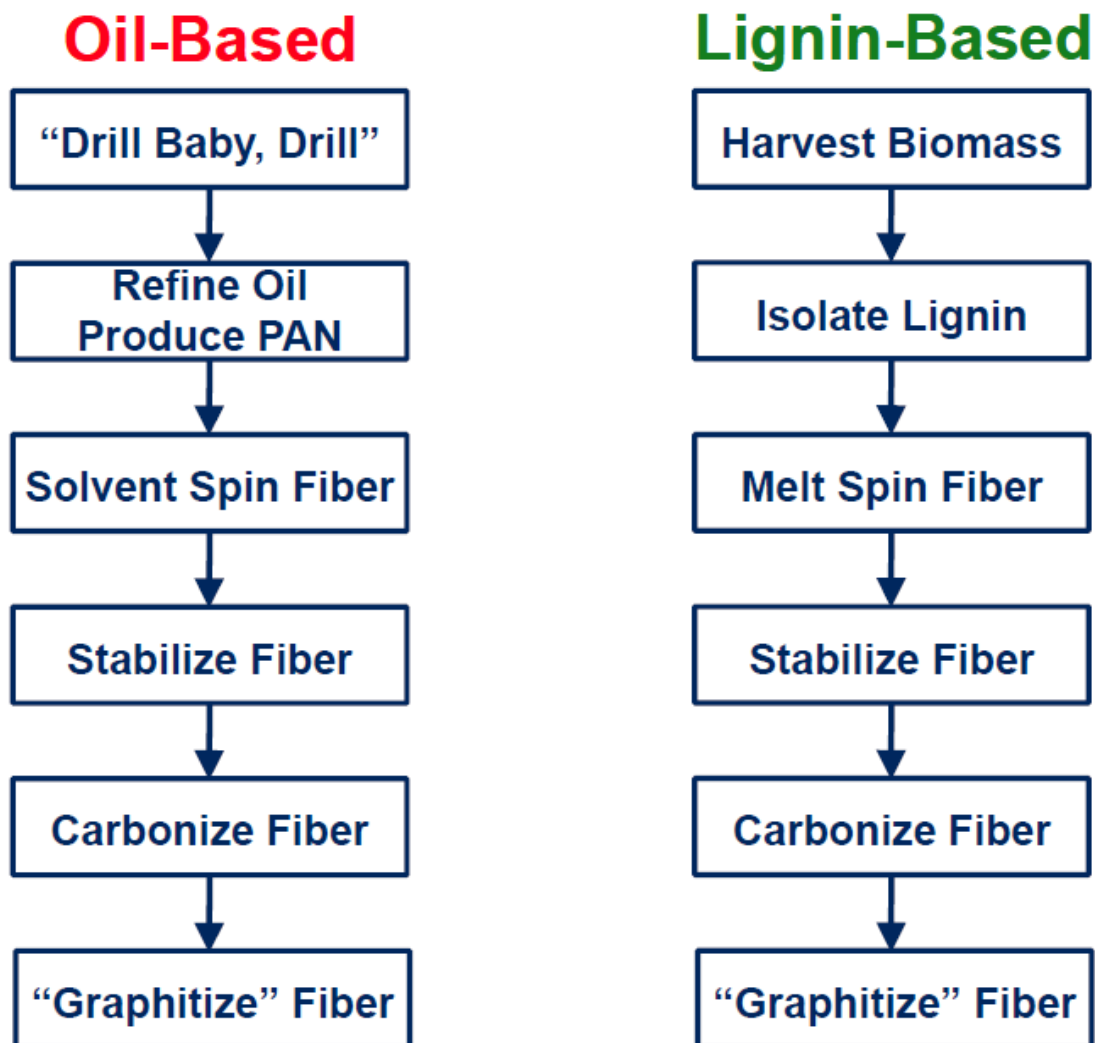


Figure 9.22: Comparing process route for lignin and oil based carbon fibre production.

Scaling

Research into the use of lignin as a precursor for carbon fibres has been based on laboratory scale. Till now the Organoslov process has not been commercialized. Most of the advanced stabilization methods proposed for lignin precursors are also in laboratory

scale. These processes must be scaled-up for commercial operations. Some researchers believe that future scale-up of lignin-based carbon fibre production should be a process very close to the conventional PAN production process to minimize the investment cost. Cost can vary by factors such as scale of production, facility location, and energy costs [131]. In the ORNL cost model [126], it was noted that the assumed 2 hours stabilization time was up to 100 hours in the pilot scale. This means that the scale of commercial operation is not yet proven [131]. This is a very large technological uncertainty contributing to the delay in lignin fibre commercialization. Scale-up is particularly challenging for lignin-based precursors because of heterogeneity of the raw material which leads to significant complexities in the melt spinning and stabilization steps.

Development of new scientific knowledge base

Despite over 60 years of lignin research, the chemistry of lignin is yet to be well understood. Lignin has a complex chemical structure which is generally dependent on biomass species, extraction process and conditions applied. Lignin is also highly inhomogeneous and polydispersed with high level of impurities. Some lignins are not susceptible to melt spinning whereas some are readily melt-spun. These create the need for the development of a wide scientific knowledge base. The understanding of lignin chemistry as it relates to carbon fibre production is dependent on this knowledge base. Moreover, the industries need a full understanding of lignin before they can appreciate the need to develop production interest. The fear of going into the unknown is a risk factor for the industries.

Recyclability

Recycling is a major issue facing the industrial applications of synthetic carbon. Government regulations on recyclability of products have forced industrialist to select raw materials. Lignin carbon fibre production is still in the developmental stage. The issue of recyclability has not yet been studied extensively. Recycling of lignin-based carbon fibres requires extensive research to identify the potential for recycling and establish process routes for complete recycling.

Target properties

Attaining target properties is another risk factor facing the production and application of lignin carbon fibres. The highest single filament tensile strength of lignin carbon fibres is 1.2 GPa with tensile modulus of 82.7 GPa against the required tensile strength of 1.72

GPa and tensile modulus of 172 GPa projected for automotive applications. The uncertainty of being able to attain this goal in the near future may cause certain industries to hold back investment in lignin based carbon fibres. However, it should be noted that the most important carbon fibre precursor, PAN was in experimental stage for over 60 years before the required properties for automotive applications was met. Investment should be committed to the understanding of the evolution of the structure of lignin carbon fibres.

9.5 Conclusion and outlook

Lignin carbon materials are becoming very useful in the society because they are obtained from sustainable resources and will contribute to fuel economy culminating in a reduction in greenhouse gas emissions. Moreover, lignin carbon materials are economic efficient and readily available from wastes sources. They are also able to reduce the cost of manufacturing by more than 80%. Carbon fibres from lignin possess appreciable properties but not yet up to the standard for automotive applications. These properties can be improved with a good understanding of the lignin complex system and the role of lignin chemistry in as it relates to carbon fibre production. In lieu of this, attention should be paid to melt processing designs, modification of lignin structure to obtain substantial increase in molecular weight with narrow distribution, lignin/bio-polymer blending and the use of linking agents and catalyst. However, with current properties, lignin carbon fibres have found usefulness in flexible carbon electrode, high performance supercapacitors, electro-catalyst, energy storage, and high-capacity and high-stability lithium ion batteries. Lignin based activated carbon are found to possess properties exceeding those from synthetic sources in terms of surface area, pore volume and distribution. They have been applied as absorbents and supercapacitors. Cost estimation of lignin carbon fibres shows that lignin carbon fibres will result in over 300% reduction in the cost of carbon fibres. Cost estimation models should be updated with current trend in lignin processing.

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