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Creating a sustainable carbon future

AUSTRALIAN CARBON INNOVATION

NEXT GENERATION CARBON PRODUCTS IN VICTORIA



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1 Executive Summary

Carbon is an extremely versatile element that is the basis for all of life on Earth. It has application across the range of human endeavour and all areas of the economic and social wellbeing of people and the planet. For much of human history, only four main types of carbon were known: diamond, graphite, carbon black (as soot) and charcoal. It is only since the second half of the 20th century that completely new forms of carbon were discovered – carbon fibres, fullerenes, carbon nanotubes and graphene – that are now used in the most advanced emerging technologies of the 21st century, e.g. aerospace, energy-efficient automobiles, wind turbine blades, flexible solar panels, energy storage (lithium ion batteries, supercapacitors), smart and wearable electronics, medical diagnostics, etc. Around the world, the race is on to capitalise on these new developments and to leverage available natural resources into competitive manufacturing industries. There is little doubt that further applications will be developed as these technologies reach technical maturity and cost reductions.

Victoria's Latrobe Valley, with its abundant carbon resources and skilled workforce, is well placed to take advantage of these new developments, to create the new industries and jobs needed for continued economic prosperity. The Latrobe Valley is home to two significant carbon resources that could support a range of new manufacturing industries, bringing high-tech jobs to a region in transition. One is the ~ 600,000 tonnes/year of waste lignin produced as a timber byproduct at the Maryvale paper mill, which is currently burned to raise steam. The other is the 33 billion tonnes lignite resource, a fossil form of lignin, which is currently burned at a rate of ~44 million tonnes per annum, to produce electricity. The key to extracting greatest value from these resources is to value them as clean sources of raw carbon, rather than only as energy sources, with the potential to be reworked into high value new materials.

In addition to the high-tech materials applications, there is also an emerging understanding of how carbon can contribute to the productivity of the agricultural sector and to the capture and retention of CO₂ into the soil. Lignite itself is well known to be a beneficial soil amendment, increasing organic carbon in depleted soils and thereby increasing plant yields and drawdown of atmospheric CO₂. Humic substances extracted from weathered lignite have found a wide range of potential applications in agriculture, including stimulation of plant growth, and solubilisation of essential plant trace elements. When used in combination with chemical fertilisers such as urea or superphosphate, humic substances reduce the amount of fertilisers required by as much as half, leading to a much better environmental outcome. Significant growth and health benefits can be achieved in the chicken, beef, pork, sheep and aquaculture industries when humic substances are added to the dietary mix. If similar levels of humic substances can be extracted from 'as mined' lignite, this would drop the production cost significantly and lead to the expansion of a major new industry sector for Victoria.

This report has been prepared by ACI to inform its members of the opportunities that exist to transform lignin and lignite into high value carbon products. It covers topics including briquettes, recovery of purified lignin, metallurgical reductants, activated carbons, humic substances, carbon fibres and graphene-based products. In each case, the approach taken is to provide a general context

for the topic, relevant local background, and a snapshot view of current research programs under way.

The report shows that a valuable body of carbon processing expertise has already been developed in the Latrobe Valley, which is supported by skilled scientists and research infrastructure in Victoria's universities and at CSIRO. All the ingredients are available for Victoria to become a world leader in the production of high value, next-generation carbon products.

There is a caveat, however. Currently 99.99% of all lignite and 100% of all lignin is used for energy production. Under current policy settings and economic imperatives it is likely that there will be no power production from lignite by the 2040's or perhaps even earlier. This means the Latrobe Region has a short period to transition from using lignite and lignins as fuels to developing their potential as raw material for advanced carbon products and agricultural applications. It is well known that it takes between 10 and 20 years to develop products from concept to commercialisation, so the transition must start now. The danger for the region is that the local expertise in carbon product manufacturing will be wasted if the opportunity is not grasped.

As with the development of the power industry in the early twentieth century this transition must be led by the State government with support by the Commonwealth government. The government of the day post-World War 1 recognised the long term need to utilise the value of lignite for low cost power production, and devoted the necessary resources to develop the technology and industry that allowed Victoria to become the manufacturing powerhouse of Australia.

What is urgently needed now is the vision and the willingness to capitalise on the opportunities highlighted in this report, and financial support for commercially-focussed research and development. The initial investment to 'kick start' these new carbon industry sectors must come from government, particularly in the research and smaller scale demonstration phases. Past experience has shown that industry will invest when the government demonstrates its confidence in the sector.

2 Introduction

The Latrobe Valley in Victoria is home to two significant carbon resources that have the potential to support a range of new manufacturing industries, bringing high-tech jobs to a region in transition. One of these resources is the waste lignin produced as a timber byproduct at the Maryvale paper mill, which is currently burned to raise steam. The other is the 33 billion tonne lignite resource, a fossil form of lignin, which is currently burned to produce electricity. The key to transforming these resources into useful products is to value them as clean sources of carbon, rather than energy sources. As sources of carbon, these resources have the potential to be reworked into new materials that underpin the advanced low-emissions technologies of the 21st century.

Carbon is an extremely versatile element that is the basis for all of life on Earth. In its pure form, carbon can take on several different bonding arrangements between atoms, resulting in different physical forms, or allotropes, with markedly different properties. These are summarised in Figure 1.1 below.

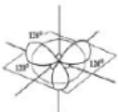
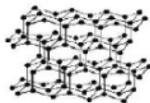
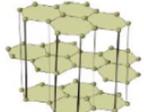
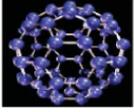
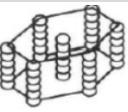
Bonding Hybridisation	Allotropes	Derived and Defective Forms
 SP²	 Cubic diamond	 Diamond  Diamond-like Carbon
 SP³	 Hexagonal graphite	 Graphite  Poly-crystalline Graphite  Carbon Black  Cokes and Activated Carbons  Pyrocarbons  Graphene
 SP^{2+ε} rehybridization	 Fullerene	 Buckminsterfullerene  Bucky Onions  Toroidal Structures  Acetylene Blacks  Nanotubes
 SP¹	 Carbyne	No derived forms yet developed

Figure 1.1: Carbon allotropes (adapted from Mochida et al. 2006)

For much of human history, only four main types of carbon were known: diamond, graphite, carbon black (as soot) and charcoal. It is only since the second half of the 20th century that completely new forms of carbon were discovered, with transformative implications: carbon fibres (1958), fullerenes (1985), carbon nanotubes (1991) and graphene (2004). Practical forms of the carbyne structure are yet to be developed.

Exploration of new functional forms of carbon is an active area of research, and new discoveries are still to be made. For example, in August 2019, scientists at Oxford University and IBM announced the creation of a new allotrope of carbon, called a cyclocarbon, consisting of a circular arrangement of 18 carbon atoms held together by alternating single and triple bonds (Kaiser et al. 2019), as shown in Figure 1.2 below.

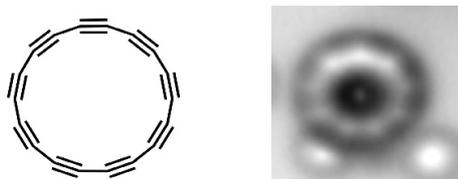


Figure 1.2: Molecular structure and atomic force microscopy image of cyclo[18]carbon (Kaiser et al. 2019)

These new allotropes of carbon are allowing the development of new, functional materials that can be used in the most advanced new technologies of the 21st century, e.g. aerospace, energy-efficient automobiles, wind turbine blades, flexible solar panels, energy storage (lithium ion batteries, supercapacitors), smart and wearable electronics, medical diagnostics, etc.

Around the world, the race is on to capitalise on these new developments and to leverage available natural resources into competitive manufacturing industries. Victoria's Latrobe Valley, with its abundant carbon resources and skilled workforce, is well placed to take advantage of these new developments, to create the new industries and jobs needed for continued economic prosperity.

This report has been prepared by ACI to inform its members of the opportunities that exist for transforming lignin and lignite into high value carbon products. Since many readers will be unaware that a history already exists in this area, this report surveys developments from the early 20th century through to the present day. The aim is to show that a valuable body of expertise has already been developed in Victoria, and there is cutting-edge work currently under way, both of which could be leveraged to bring further economic benefit to the State.

Given the diverse range of forms that carbon can take, it is not possible to cover the full spectrum in this report. Instead, this survey is limited to forms of carbon that could be competitively produced from Victorian lignin or lignite. The chapters that follow cover topics including briquettes, recovery of purified lignin, metallurgical reductants, activated carbons, humic substances, carbon fibres and graphene-based products. In each case, the approach taken is to provide a general context for the topic, relevant local background, and a snapshot view of current research programs under way.

Highlighting the range of opportunities that exist for producing next-generation carbon products in Victoria makes it evident that the Latrobe Valley is well positioned to play an important role in supplying the high performance materials that underpin the technologies of the 21st century. What is needed is the vision and the willingness to capitalise on these opportunities and position Victoria at the forefront of these developments.

3 Briquettes

To date, the largest volume value-added carbon product produced in Victoria has been briquettes, produced from Victorian lignite. Investigations into briquette production began following World War 1, and were based on adapting German technology that had been in use for over 70 years. The first commercial briquette production in Victoria commenced in 1924 at the Yallourn Power Station. The process was based on German ram extruder technology which enabled hard compacts to be made from lignite without the addition of binders (Allardice & Newell 1991). As illustrated in Figure 3.1 below, the lignite is crushed to a maximum grain size of about 5 mm, dried to a moisture content of about 14%, and under heavy pressure is consolidated in briquetting presses to blocks of shapes and sizes which vary according to the needs of consumers (Herman 1952).

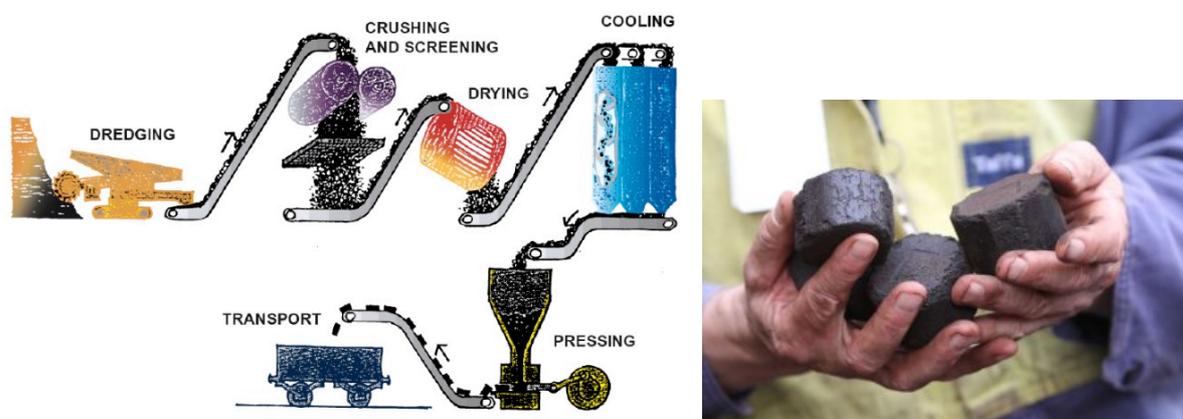


Figure 3.1: Binderless lignite briquetting (Allardice 2015)

Although in principle the briquetting process is quite simple, successful operation at the scale needed to achieve commercial viability required the development of elaborate and expensive plant suited to the characteristics of Victorian lignite. The briquette factory included equipment for crushing, screening, drying, cooling, pressing, dust control, steam boiler, power, conveying and loading, each of which had to be optimised by local engineers and scientists (Herman 1952).

Based on the experience at Yallourn, the State Electricity Commission of Victoria (SECV) began construction of the new Morwell Power Station and Briquette Factory in 1949. This was the centrepiece of the Victorian Government's post-WW2 strategy to revitalise Victoria's industrial and economic growth through the development of the Latrobe Valley into the state's principal power and energy producing region. The first commercial briquette production commenced in December 1959, producing 1.2 Mt/y briquettes and 170 MW electricity. The briquettes were used for domestic and industrial use, as well as town gas production for Melbourne at an adjacent gasworks by the Gas and Fuel Corporation of Victoria.¹

¹ <https://vhd.heritagecouncil.vic.gov.au/places/200429>



Figure 3.2: Morwell Power Station and Briquette Factory, with gasification plant in background (Allardice 2015)

To the shock of those involved, it was soon discovered that the lignite from the Morwell open cut mine, with its high alkali and sulphur content, was not suitable for briquetting. The briquettes deteriorated quickly and fouled the boilers. After only one month, production was switched to Yallourn coal supplied by a dedicated inter-connecting railway between the Yallourn and Morwell works areas (Allardice & Newell 1991).

Victorian lignite briquettes have been used in a variety of combustion applications, in domestic open fires, convection room heaters and hot water services to large steam boilers. Brick kilns were fired by briquettes in crushed form and clay product dryers used hot gases for direct drying. The predominant industrial use for briquettes was to fuel steam and hot water boilers (Allardice & Newell 1991).



Figure 3.3: Remnant of a by-gone era, Princes Hill, Melbourne

At the Gas and Fuel Corporation gasworks in Morwell, up to 180,000 t/y of briquettes were used in a Lurgi gasification plant at Morwell to produce gas for Melbourne, and some country towns (Allardice & Newell 1991).

Since the 1960s, the demand for briquettes suffered a decline due to competition from oil, electricity for domestic heating, and the discovery of natural gas in Bass Strait. The original Yallourn briquette factory ceased production in 1970 (Allardice & Newell 1991). The Morwell power station and briquette works were split from the SECV in November 1993, creating a new government business enterprise called Energy Brix Australia. At that time production of briquettes for industrial and domestic markets was about 750,000 t/y (Guy & Perry 1992).

The Energy Brix briquette factory eventually ceased operation in August 2014.² However, the closure was forced by the shut-down of the Energy Brix power station, which provided heat for drying the lignite, and not by a lack of demand for briquettes. A domestic market for briquettes still exists, and is currently being addressed by ECT (see Section 5.3 below) and by parties interested in restarting the Morwell briquette factory.

Although briquetting may appear to be an old-fashioned and out-of-date technology, it is actually a key enabling technology for the production of value-added products such as metallurgical char and activated carbon, as discussed below. It is also possible to produce briquettes from biomass, as a low-emissions fuel source or for further upgrading. Briquetting is both an important part of Victoria's industrial past and an underpinning technology for carbon upgrading, and as such may be expected to play a role into the future.

² https://en.wikipedia.org/wiki/Energy_Brix_Power_Station

4 Papermaking Lignin

4.1 PAPERMAKING IN THE LATROBE VALLEY

Papermaking is the largest carbon-based product manufacturing process in Victoria, which takes place at Australian Paper's Maryvale Mill in the Latrobe Valley. Australian Paper has been making paper in the Latrobe Valley since 1938. It currently processes about 1.7 million t/y of wood and recycled paper, transforming it into more than 600,000 t/y of office and printing papers, envelopes, bag, sack, lightweight packaging and industrial papers. The site currently includes 5 paper machines, 3 pulp mills and 2 waste paper recycling plants.³

The fundamental process of paper-making is very simple – take a diluted slurry of wood fibres in water, filter it through a fine mesh so that the water drains away, press the wet mat of fibres to remove most of the remaining water, and then allow it to dry. Paper has been made this way for nearly 2000 years following its invention in China in 105 AD.

Apart from water, wood is typically composed of about 45% cellulose, 25% hemicelluloses, 25% lignin and 5% extractives (other organic matter). Cellulose and hemicellulose are the desirable materials for paper-making and are found in the fibres. To make paper, the fibres must first be extracted from the wood, breaking the lignin bonds to free the fibres in the pulping process. The resulting pulp is a dispersion of separated wood fibres and water, whereas papermaking is the refining of pulp into dried paper.

There are a number of different wood pulping processes in commercial use, but the predominant method is the Kraft process, used by 96% of total production (Tribot et al. 2019) including at Australian Paper. In the Kraft process, woody biomass is treated at 140–180°C with an aqueous mixture solution of sodium hydroxide and sodium sulphide (also known as 'white liquor') at a high pH (≈ 13) for 2–4 h. This harsh treatment dramatically breaks the structure of native lignin, producing a 'black liquor' comprising sulphur-containing lignin.

The Kraft pulping process can be divided into two parts: the first one is called fibre line and the second one chemical recovery. The purpose of the fibre line is to process the wood into pulp for paper making. The chemical recovery regenerates the chemicals needed in the digester of the fibre line, but it is also important for manufacturing byproducts, saving energy and environmental aspects. Figure 4.1 below illustrates an overview of the combined Kraft pulp and paper making process.

³ <https://www.australianpaper.com.au/>

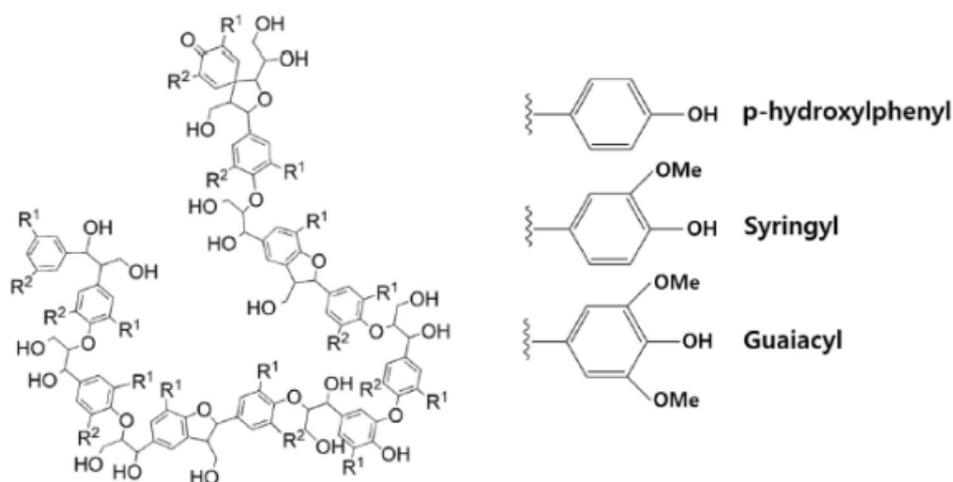


Figure 4.2: Scheme depicting a) the general chemical structure of lignins and b) the chemical structure of 3 major monomers composing lignins (Choi et al. 2019)

Globally, the pulp and paper industry extracts 50–70 million t/y of lignin from wood, but about 98% of the lignin produced in papermaking is combusted on-site for energy generation. Only 2%, about 1 million t/y of liginosulfonates from sulphite pulping and less than 100,000 t/y of Kraft lignins are commercially exploited. Two prominent commercial lignin upgrading operations are vanillin production from liginosulfonate (Borregaard, Norway) and dimethyl sulfoxide from Kraft lignin (Gaylord Chemical, USA) (Calvo-Flores & Dobado 2010).

Other commercial uses of lignin make use of its polymer and polyelectrolyte properties. Kraft lignin products are generally used in high end applications such as in foam fire extinguishers, to stabilize the foam and in printing inks for high speed rotary presses, as an extender/modifier, and as reinforcement pigment in rubber compounding. After modifying base lignin, it can be used as emulsifying agents/emulsion stabilizers, as sequestering agents like pesticide & dye dispersants, additives in alkaline cleaning formulations, complexing agents in micronutrient formulations, flocculants, and extenders for phenolic adhesives. Such uses comprise about 75% of the commercial lignin products. Other, minor applications include adhesives and fillers (Agrawal et al. 2014)

There is currently a strong international emphasis on the development of lignin as a sustainable precursor for carbon-based products. This has led to the 'biorefinery' concept, in which sustainable wood and grasses are transformed into ethanol, fuels and chemicals. In this light, lignin offers great potential as a building block for a wide range of high-value products, such as phenolic resins, surfactants, epoxy resins, adhesives and bioplastics. Chemical modification of lignin can create a wide range of value-added product opportunities, as illustrated in Figure 4.3 below.

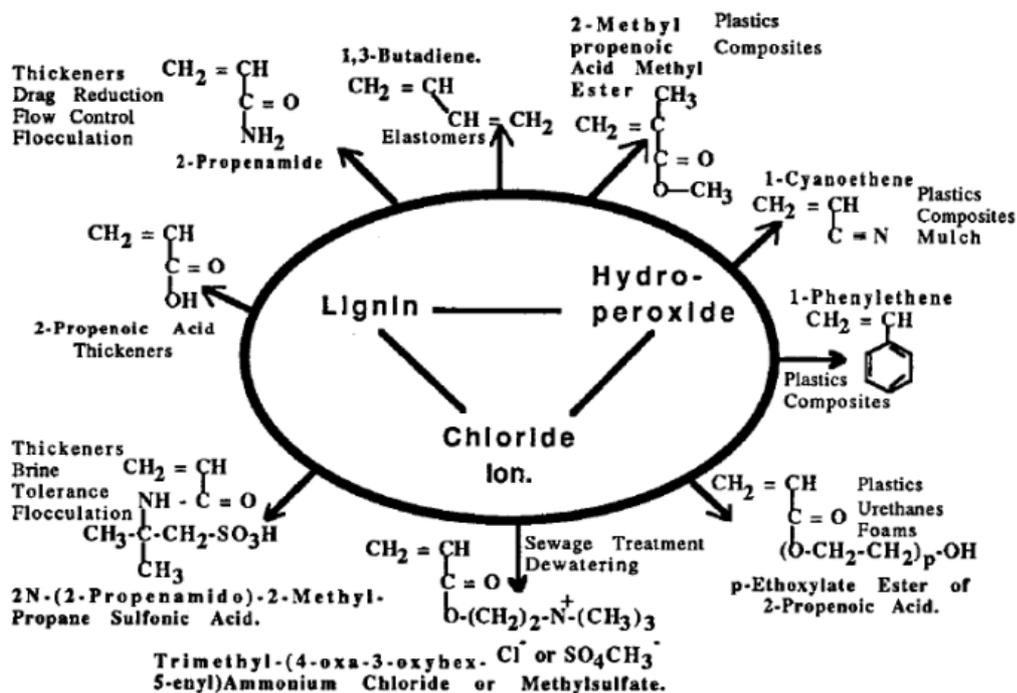


Figure 4.3: Monomers that may be grafted onto lignin and uses of the resulting products (Meister 2002)

A major research focus in recent years has been on fabricating carbon fibres and activated carbon fibres using lignin as a precursor. This work is discussed in Section 8 below.

4.3 RECOVERY OF LIGNIN

Kraft lignin can be recovered from the black liquor by precipitation with acid. This is predominantly performed by using either carbon dioxide or a mineral acid (e.g., sulphuric acid) or a combination of the two to drop the pH of the black liquor from approximately 13–13.5 to 9–10. After acidification, the lignin is usually filtered using a belt filter or a filter press and washed with acid (e.g., sulphuric acid) and water, as shown in Figure 4.4 below, to produce what is known as ‘technical lignin’ (Kouisni et al. 2012).

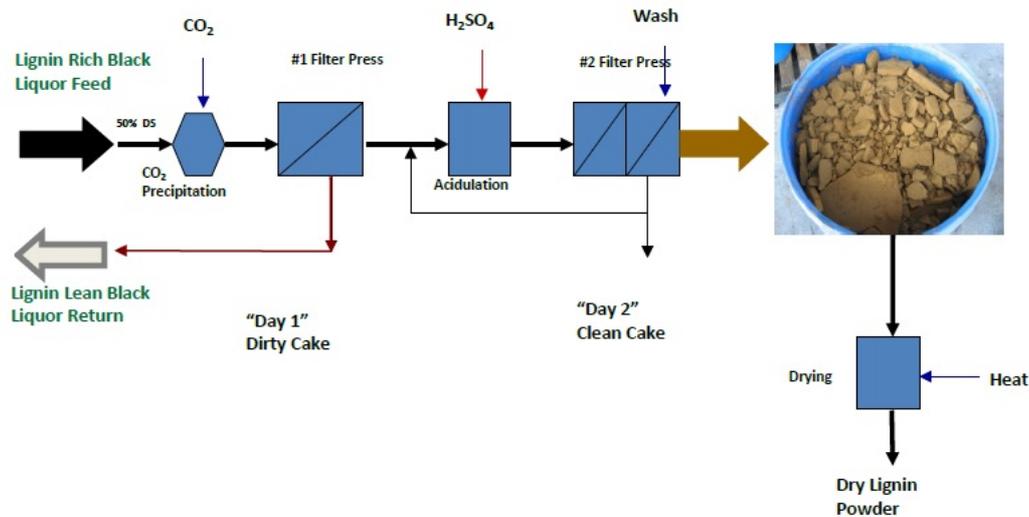


Figure 4.4: Recovery of technical Kraft lignin from black liquor (Husman 2012)

Kraft lignin is a hydrophobic material with a lower molecular mass than the original lignin. The treatment yields a lignin that is highly modified, water-insoluble, and soluble in a strong aqueous base. Kraft lignins contain sulphur up to 3wt%, in the form of thiols, thioethers, etc. (Frank et al. 2014).

The residual ash content and other impurities present in commercially-available technical lignins has an adverse effect on their ability to be used in fabrication of advanced carbon materials such as carbon fibres. This has led to the investigation of processes for recovering purified lignin from process black liquors.

The best developed of these, called LignoBoost (shown in Figure 4.5 below), involves filtering the precipitated lignin and redispersing the filter cake by aqueous acid followed by filtration and washing. The ash content of Kraft lignin from this process can be ~0.2wt%. The LignoBoost process has been verified on a scale of about 4,000 t/y, in a demonstration plant located in Bäckhammar, Sweden, owned and operated by Innventia (Tomani 2010).

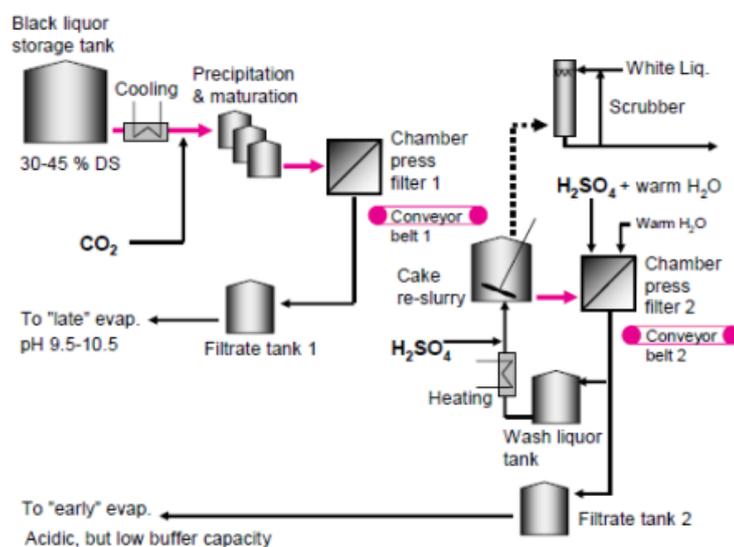


Figure 4.5: General layout of the LignoBoost lignin recovery process (Tomani 2010)

Recently, Thies et al. (2018) patented a process using hot aqueous acetic acid to purify and fractionate black liquor resulting in an “ultrapure” lignin with an ash content lower than 0.1 wt% and sodium content <50 ppm. In the so-called Aqueous Lignin Purification with Hot Acids (ALPHA) process, Kraft lignin is combined with hot acetic acid–water mixtures under appropriate conditions, forming two equilibrium liquid phases, with the metal salts being extracted into the solvent-rich phase and an ultraclean, lignin-rich phase being obtained as the desired product. The solvent composition can be “tuned” to partition the feed lignin between the solvent-rich and lignin-rich liquid phases according to molecular weight (Klett et al. 2015).

ALPHA was originally conceived as a two stage batch reaction process, but it was found that condensation polymerisation reactions occurred in the solvated, lignin-rich liquid fraction at the elevated temperatures (e.g., 60–100°C) of operation, significantly increasing the lignin molecular weight. The process was subsequently configured for continuous-flow operation, as shown in Figure 4.6 below. Residence times in this system are no more than 20–30 s, essentially eliminating condensation reactions (Klett et al. 2016).

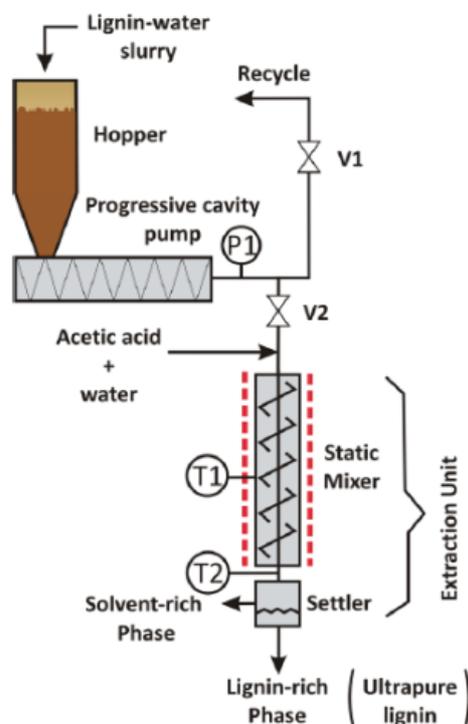


Figure 4.6: Schematic of the continuous process used to produce ultrapure lignin (Klett et al. 2016)

Even with these improved purification processes, Kraft lignin contains covalently-bonded sulphur impurities which cannot be eliminated and may render the lignin unsuitable for some applications. To counter this problem a family of alternative processes have been developed, called Organosolv, which involve extraction of lignin with an organic solvent/water mixture at a high temperature/pressure. The most widely used solvents are alcohols, together with other mixtures of solvents and reagents. Lignin is isolated by acid precipitation. The two commercially available Organosolv lignins are Alcell and Organocell lignins. Organosolv lignin has a less modified structure than Kraft lignin, and is sulphur-free (Calvo-Flores & Dobado 2010). The Organosolv process is of increasing interest because it produces pure, sulphur-free lignin with low ash content, but is currently conducted at relatively small scale (Frank et al. 2014). It has been tested in pilot scale in Canada (Lignol Innovations Ltd, producing HP-L lignins), in France (CIMV, producing Biolignin) and Germany (Dechema/Fraunhofer) (Souto et al. 2018).

4.4 VICTORIAN RESEARCH CONTEXT

4.4.1 Carbon Negative Biorefinery

Federation University at Churchill has developed the concept of a Carbon Negative Biorefinery to create value-added products from the agricultural resources produced in the Latrobe region. The Carbon Negative Biorefinery has the potential to generate a wide variety of products, such as

construction materials, feedstock chemicals, biodegradable polymers, fuels, fertilisers and carbon fibres.

The Carbon Negative Biorefinery concept comprises a number of different units. Figure 4.7 below shows the process flow for Unit 1, which produces C₂ and C₄ platform chemicals. Succinic acid (C₄) is used for biodegradable plastics and other polymers while acetic acid (C₂) is used for biofuels and polymers.

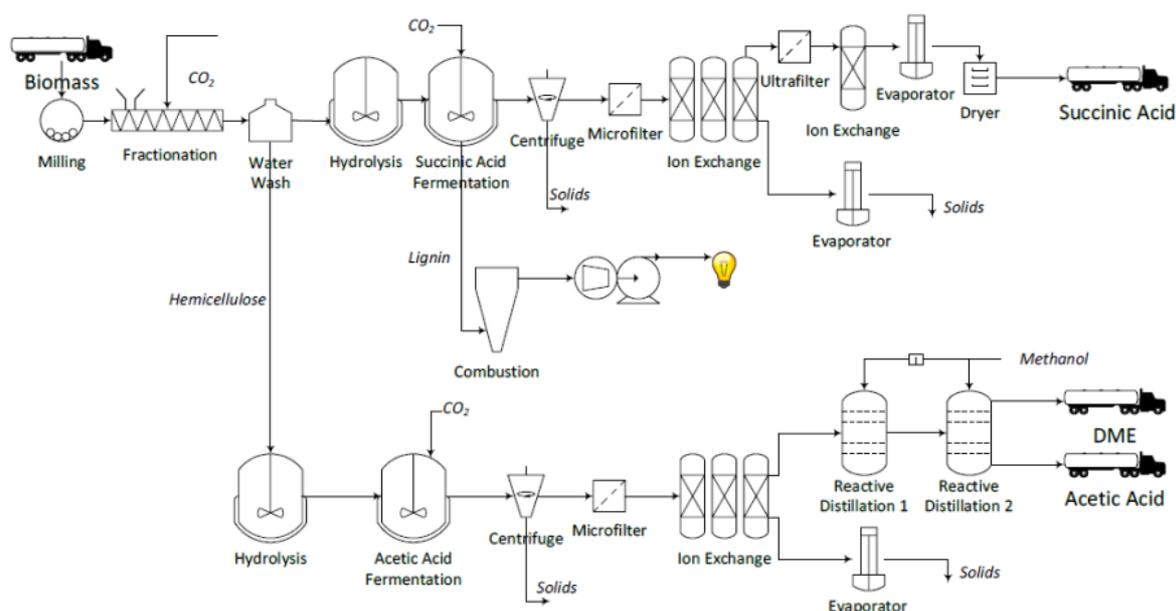


Figure 4.7: Unit 1 of the Carbon Negative Biorefinery (© Adeel Ghayur)

Federation University is proposing to develop the concept of the Carbon Negative Refinery through laboratory research and university coursework development.

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4.4.2 ARC Research Hub for Processing Lignocellulosics into High-Value Products

Australian Paper is a participant in the Australian Research Council (ARC) Hub for Processing Advanced Lignocellulosics into Advance Materials, which was launched in October 2018. The ARC Hub aims to convert renewable and readily-available lignocellulosic material and waste streams from the Australian Pulp, Paper and Forest Industry, into new, high-value products in demand in existing and developing markets. Along with Australian Paper, the other consortium members are Orora, Norske Skog, Visy, Circa, Leaf, Monash University, the University of Tasmania, the University of South Australia, the Government of Tasmania and AgroParis.

A total of \$6.8 million over five years will be invested to convert materials, such as wood, plant-based matter and other biomass, into marketable chemicals and materials such as cellulose-based hydrogels for personal medicine (blood typing), nanocellulose films to replace plastic food packaging, and nanogels to help farmers maintain crops in the ever-changing climate.

This industry transformation will be achieved through three specific objectives:

- Derive 'green' chemicals from Australian wood and lignocellulosic streams: Following examples in Europe and North America where high-grade chemicals, including gels and thermoplastics, are developed from wood extractives;
- Engineer new nanocellulose applications: Using Australian agricultural and wood residue to create nanocellulose and better nanofibers; and
- Develop ultralight paper and novel packaging: Creating cellulosic-based packing products with significantly improved physical properties and new attributes, including radio-frequency identification technology to integrate with transport / retail information systems.⁶

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⁶ <http://pals.biopria.com.au/australian-paper-industry-gets-bio-overhaul-thanks-to-new-research-hub/>

5 Metallurgical Reductants

In metallurgy, metal is recovered from an ore by heating in the presence of a reductant, which is typically carbon. Perhaps the best known example is in ironmaking, where iron metal is produced by reacting iron oxide with carbon-rich coke, derived from coal. Each metallurgical process imposes different requirements on the carbon products used as reductants, such as softening, swelling, fusion and porosity in coke and char making; reactivity, electrical resistivity and carbon consumption of the carbon anodes in electric arc furnace; and strength related to overburden pressure in blast furnaces.

This chapter discusses the progress made in developing applications for Victorian lignite as a metallurgical reductant. These include the production of char products for use in ferroalloy production and recarburising of steel, production of carbon anodes for aluminium smelting, and as replacements for coke in ironmaking.

5.1 CHAR PRODUCTS

During the 1950s and 1960s, researchers at the Gas and Fuel Corporation of Victoria attempted to produce a metallurgical char from Victorian lignite. The focus of the research was to use binderless briquettes, as produced at the Yallourn briquette factory, as a precursor for carbonisation. The major problem encountered was that the briquettes cracked during carbonisation. After much trial-and-error experimentation, it was determined that the rate of temperature increase during carbonisation must be controlled to ensure that the differential shrinkage between the surface and core of the briquettes should vary as little as possible. This led to the development of an “ideal heating cycle” devised by Higgins and Kennedy (1966) and later refined and implemented in a commercial moving-bed vertical retort by Kennedy (1971). The “ideal heating cycle” involves carefully timed heating of Yallourn briquette feedstock in nine temperature zones, to control the rate of evolution of volatiles and avoid the severe shrinkage and size degradation which can occur, particularly at around 100°C (drying) and 400°C (onset of devolatilisation).

A commercial plant based on a modified Lurgi design, utilising the “ideal heating cycle” commenced production in 1970 (Guy & Perry 1992). This plant, operated by Australian Char Pty Ltd (shown in Figure 5.1 below), produced 80,000 t/y of char from 180,000 t/y briquettes (Allardice 2015).

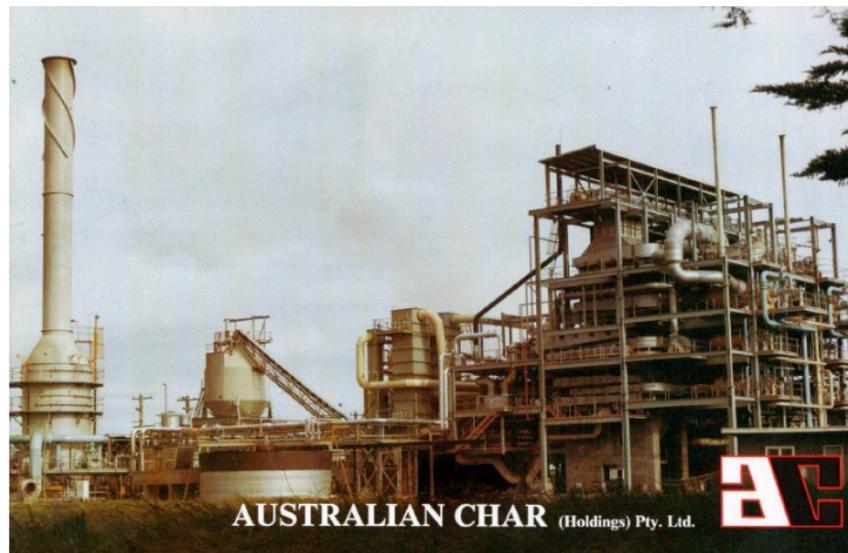


Figure 5.1: Australian Char briquette carbonisation plant in Morwell (Allardice 2015)

The special properties of the char made it suitable for a number of applications, including ferroalloy production, recarburising of steel, reductant of mineral sands, as a carbon feedstock for carbon disulphide and calcium carbide manufacture, for production of 'Heat Beads' barbecue fuel, and for preparation of activated carbons (Guy & Perry 1992).



Figure 5.2: 'Heat Beads' barbecue fuel manufactured from lignite char

The AusChar carbonisation plant was closed down in 2014, following the closure of the Morwell briquette factory which supplied raw materials for char, but there are currently commercial parties interested in restarting operations.

5.2 CARBON ANODES FOR ALUMINIUM SMELTING

5.2.1 The demand for carbon materials in the aluminium industry

Production of carbon anodes for use in aluminium smelting was a topic of research interest in Victoria during the 1960s, '70s and '80s. This application represents a potentially high-volume, high-value market for Victorian lignite.

Aluminium is produced industrially using the Hall–Héroult process, involving electrolytic reduction of aluminium oxide (alumina), shown in Figure 5.3 below. The electrolyte is made up of molten cryolite (sodium hexafluoroaluminate) and other additives, and is contained within a carbon and refractory lining inside a steel shell. The cathode for the electrolytic process is a carbon lining made up of pre-formed carbon cathode blocks. The anode for the electrolytic process is a large carbon block held by a metal frame and suspended in the molten cryolite/alumina mixture to conduct the current. A strong electrical current of 200 – 400 amps is passed through the cell, causing oxygen in the alumina to react with the carbon anodes, creating carbon dioxide. At the same time, hot liquid aluminium is separated from the oxygen and sinks to the bottom of the reduction cell.

A strong electrical current is then passed through the reduction cells. The current causes oxygen in the alumina to react with the carbon anodes, creating carbon dioxide. At the same time, hot liquid aluminium is separated from the oxygen and sinks to the bottom of the reduction cell.

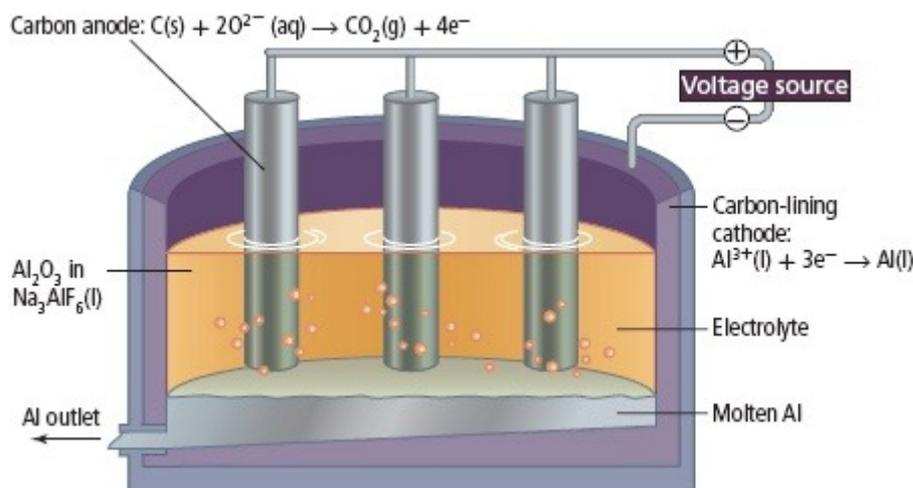


Figure 5.3: Hall-Héroult electrolysis process for aluminium smelting⁷

The carbon anodes used in this process are usually manufactured from calcined petroleum coke (CPC) and coal tar pitch (CTP), and have a working life of around 26 days before needing to be replaced. To produce one tonne of primary aluminium, a smelter needs about 425 kg of carbon anode which is produced by mixing 80% of CPC and 20% of CTP. In 2018, total global production of

⁷ <https://www.quora.com/What-are-some-applications-of-Electrolysis-in-the-field-of-metallurgy>

aluminium was 64,336,000 tonnes.⁸ This equates to a consumption of about 21.8 million tonnes of CPC and 5.5 million tonnes of CTP.

The primary aluminium smelting industry is currently experiencing financial pressure because of the rising cost of CPC and CTP. The costs of these two ingredients have increased by over 80% in less than two years. As a result, alumina, coke and pitch accounted for around 50% of the smelters' cost base in 2018. This does not appear to be a short-term price bubble, but part of a long-term upward trend in coke and pitch prices, as shown in Figure 5.4 below.

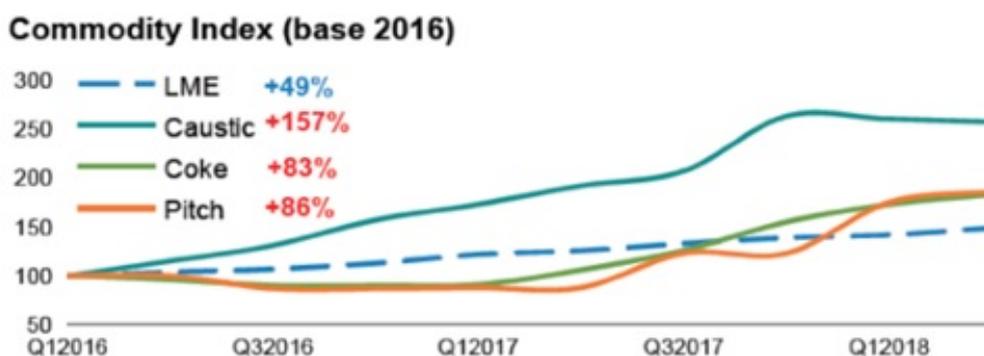


Figure 5.4: Upward trend of coke and pitch prices⁹

Calcined anode grade pet coke is produced from low/medium sulphur green pet coke (GPC) (“green”-unprocessed), which is a by-product of refining low sulphur medium and heavy crude oil. Currently, there is no known commercially viable substitute for calcined petroleum coke in the anodes used in aluminium smelters. It boasts a superior combination of electrical conductivity and resistance to chemical and physical degradation in the smelting pot, which contains lower levels of contaminants (i.e. ash). China produces 75% of the CPC used in aluminium production, but is using more of this material for steelmaking. As a result, the Chinese CTP supply continues to shrink with no new meaningful supply source in sight.¹⁰

Coal tar pitch is a key raw material to make the products defining the “post-carbon” high tech renewable economy: Lithium Ion batteries, LED lights, solar panels and carbon fibre. These markets are still small but growing rapidly. While the aluminium industry is the biggest consumer of CTP (some 90%), other applications (e.g. electric arc furnace electrodes and tech renewables) are valued more highly, putting upward pressure on prices.¹¹

This combination of market forces is creating a strong incentive to develop lower-cost alternatives to CPC and CTP, creating a potential opportunity for Victorian lignite.

⁸ <http://www.world-aluminium.org/statistics/#data>

⁹ <https://aluminiuminsider.com/why-are-anode-production-costs-rising/>

¹⁰ <https://aluminiuminsider.com/why-are-anode-production-costs-rising/>

¹¹ <https://aluminiuminsider.com/why-are-anode-production-costs-rising/>

5.2.2 Manufacture of carbon anodes from lignite

5.2.2.1 Specifications for aluminium industry anodes

The performance specifications of carbon anodes suitable for use in the aluminium industry are shown in Table 5.1 below.

Anodes	
Bulk density	$\geq 1.6 \text{ g/cm}^3$
Resistivity	$\leq 0.006 \text{ } \Omega \cdot \text{cm}$
Compressive strength	$\geq 38 \text{ MPa}$
Anode carbon consumption	$\leq 115\%$
Air burn	$0.17 \text{ g/cm}^2 \text{ at } 650^\circ\text{C}$
CO ₂ reactivity	$0.02 \text{ g/cm}^2 \text{ at } 950^\circ\text{C}$
Aggregate	
Ash content	0.2- 0.7%, depending on metallic limits, e.g. Al 15-100ppm, B 0.2-0.7 ppm, Ca 25-500 ppm, Fe 50-500 ppm, Mg 10-250 ppm, Si 10-700 ppm, Ti 2-60 ppm, V 5-1000 ppm, S 0.2-6.0 wt%
Powder bulk density (-8+14#, Tyler, as poured)	0.8 g/cm^3
Skeletal density (0.4nm)	$1.88 - 2.11 \text{ g/cm}^3$
Electrical resistivity (-30+60#, Tyler, compressed at 10MPa)	$0.11 \text{ } \Omega \cdot \text{cm}$
Binder (coal tar pitch)	
Cube-in-air softening point	$108 - 112^\circ\text{C}$
Density	$1.336 \text{ g/cm}^3 \text{ @ } 25^\circ\text{C}$
Quinoline insoluble	$12 - 17 \text{ wt}\%$
Ash content	$0.25 \text{ wt}\%$
Sulphur content	$0.1 - 6.5 \text{ wt}\%$

Table 5.1: Typical parameters for good aluminium industry anodes (Gardner et al. 1986)

These values provide a benchmark against which alternative anode materials can be assessed. There are good reasons to expect that these specifications could be met by aggregate and/or pitch produced from Victorian lignite.

One reason for doing so is that an electrode-quality char is produced in Germany by Rheinbraun Brennstoff from Rhenish lignite. This product, called Lignite Special Coke is claimed to have favourable heat-conductive properties, high specific electrical resistance, low sulphur content and ability to absorb harmful gases, making it the ideal raw material for manufacturing electrodes. Rheinbraun Brennstoff says that Lignite Special Coke is not affected by volatile commodity prices on the world market, and long-term supply agreements make costs easier to predict, thus making

electrode manufacturing more profitable.¹² No information was findable on the specifications for Lignite Special Coke, or on its use in specific applications.

Another reason is that promising results have already been published for both Texas lignite and Victorian lignite, as described below.

5.2.2.2 Experience with Texas lignite

During the 1960s, researchers at the Bureau of Mines, U.S. Department of the Interior, investigated the production and upgrading of pitch from Texas lignite. Crude tar was produced by fluidised bed carbonisation of lignite at about 500°C, and the pitch was the residue from distillation of the tar under vacuum at 350°C (Berber et al. 1967).

The pitch was further upgraded to produce both coke and binder for use in aluminium smelting anodes by two methods – thermal cracking (Berber et al. 1967) and delayed coking (Berber et al. 1968). Both methods produced an oily liquid and coke. The liquid was distilled into a distillate and residue, the latter being employed as an electrode binder. The coke from both processes was leached in dilute acid, calcined at 1370°C and screened for use as electrode aggregate (Berber et al. 1969).

It was found necessary to calcine the ‘green’ coke to make it suitable for use, for several reasons. First, when ground the green coke could not be bound together to give a proper density. Second, electrodes were difficult to mould or extrude from green coke. Third, the electrodes gave off volatile matter during baking, resulting in a very porous product. Finally, electrodes prepared from green coke had a high resistivity and were poor conductors of electricity (Berber et al. 1969).

It was found that anodes could be prepared entirely from lignite-derived coke and binder, exhibiting compressive strength of up to 37 MPa and electrical resistivity of 0.007 – 0.009 Ω.cm. After electrolysis testing, the surfaces of these anodes were very similar to those of anodes made from commercial materials. The surfaces were uniformly eroded and the electrolyte covered the entire surface, indicating good wettability (Berber et al. 1969).

These results were promising, coming close to the performance expected of commercial anodes. The anodes produced with lignite coke were found to contain more and larger void spaces than those produced with petroleum coke. It was shown that the density could be increased and the electrical resistivity reduced by using higher calcination temperatures.

A patent was taken out for the manufacturing process (Berber & Rice 1974), with the expectation of making further performance improvements. However, the low cost and ready availability of calcined petroleum coke at that time meant that the process was not commercially viable, so further development work was discontinued.

¹² <https://www.rheinbraun-brennstoff.de/en/products-for-industry-and-the-environment/lsc-lignite-special-coke/electrode-manufacturing/>

5.2.2.3 Experience with Victorian lignite

Researchers at the University of Melbourne investigated the use of lignite char in the fabrication of anodes for aluminium smelting during the 1960s. It was found that the porosity of char produced from commercial briquettes at 1200°C was 5% lower than that of petroleum coke (Evans & Hermann 1970). However, the ash yield from commercial briquette char (3-4 wt%) was too high, but this could be reduced to an acceptable level by acid washing (Bull 1965).

While satisfactory anodes could not be produced using acid-washed briquette char alone, it was found that good performance could be achieved with electrodes containing 20 – 50 wt% lignite char as a partial substitute for petroleum coke. The best results were achieved using a blend of 20% acid-washed lignite char and 80% petroleum coke, with pitch comprising 19 wt% of the electrode (Cullen et al. 1973). A comparison of the data obtained in an alumina cell with this formulation and that with 100% petroleum coke is shown in Table 5.2 below.

	Petroleum coke	20% Lignite coke
Bulk density, g/cm ³	1.49	1.44
Resistivity, Ω.cm	0.0051	0.0054
Compressive strength, MPa	34.2	37.9
Anode carbon consumption, %	107	110
Ratio of carbon consumed to aluminium produced	0.51	0.45
Current efficiency, %	70.5	81.5

Table 5.2: Properties and alumina cell performance for anodes prepared from petroleum coke and 20% lignite char with petroleum coke (Cullen et al. 1973)

The anode including lignite char performed better on most measures, although the bulk density was slightly low and the electrical resistivity was slightly high. On the other hand, the carbon consumption rate was lower, so more aluminium could be produced from a given anode. This was a very promising result, and it would be good to see an economic analysis of the potential benefits of using lignite char as a partial replacement for petroleum coke. However, any such analysis at the time was not published, and research at the University of Melbourne was discontinued.

Research on this topic was subsequently taken up at the CSIRO Division of Mineral Chemistry. It was found possible to increase the bulk density of the anodes by impregnating lignite char with pyrolytic carbon deposited from methane, but the pyrolytic carbon did not bond to the char and increased the rate of carbon consumption (Gardner et al. 1976). A systematic study of different char preparation methods, carbon impregnation and binders was unable to produce a bulk density matching that of petroleum coke. It was concluded that most of the problems were due to the microporosity of lignite which persisted through the charring stage, even after calcination. While the air burn of char anodes

was 30% lower than petroleum coke anodes, the anode carbon consumption rate was higher, so overall carbon consumption was higher for char than coke anodes. It was recommended that utilisation of char in aluminium smelting anodes should be postponed until there is a restriction in the supply of petroleum coke (Gardner et al. 1986).

5.2.3 Victorian Research Context

The CSIRO study marked the end of carbon anode research in Victoria, despite the generally promising results that had been achieved. Since that time, calcined petroleum coke (CPC) has remained the mainstay of the carbon anode industry. However, the aluminium smelting industry is currently experiencing difficulties due to the falling availability and rising price of CPC. At the same time, steady demand growth in Asia and the growing application of aluminium in the auto and aerospace industries is expected to increase aluminium consumption from 62.9 Mt in 2019 to 79.7 Mt by 2028.¹³ This suggests that there may now be a market opportunity for acid-leached Victorian lignite char as a partial replacement for CPC in aluminium smelting electrodes.

It is recommended that a cost analysis study be undertaken in consultation with Australian aluminium smelters, to determine whether there would be sufficient cost incentive to allow commercial consideration of a lignite char alternative. If this looks promising, then a trial evaluation program could be undertaken in collaboration with smelters fabricating anodes in-house.

5.3 MATMOR PROCESS

During the 1980s, researchers at the University of Melbourne developed a method for transforming run-of-mine Victorian lignite into a dense, dry, hard product. The researchers found that raw lignite could be comminuted in a kneader to break down its structure, releasing water to form a paste-like material. The paste could be extruded to form pellets which, when dried at or near ambient conditions, formed a hard briquette-equivalent product. It was found that the product strength could be improved with the addition of pH modifiers (Johns et al. 1984). For maximum strength, the pellets had to be dried slowly at near-ambient temperature, to avoid weakening the structure by stress-induced cracking (Johns et al. 1989).

This technology forms the basis for what is now known as the 'Coldry process', which is being championed by Environmental Clean Technologies Ltd (ECT). The company is presently pre-commercial, relying on a combination of market-based capital raising and government funding via the Australian Government's R&D Tax Incentive program to fund its programs.¹⁴ The Coldry process, shown in Figure 5.5 below, has been scaled up to a 16,000 tonne/year pilot plant at Bacchus Marsh. ECT developed a specialised dryer to dry the moist pellets, designed to use low-grade waste heat to facilitate slow drying at temperatures of less than 80°C (Wilson 2005).

¹³ <https://www.mining.com/global-aluminium-market-remain-undersupplied-coming-years-report/>

¹⁴ <http://www.ectltd.com.au/technology-commercialisation-strategy-and-revenue-model-overview/>

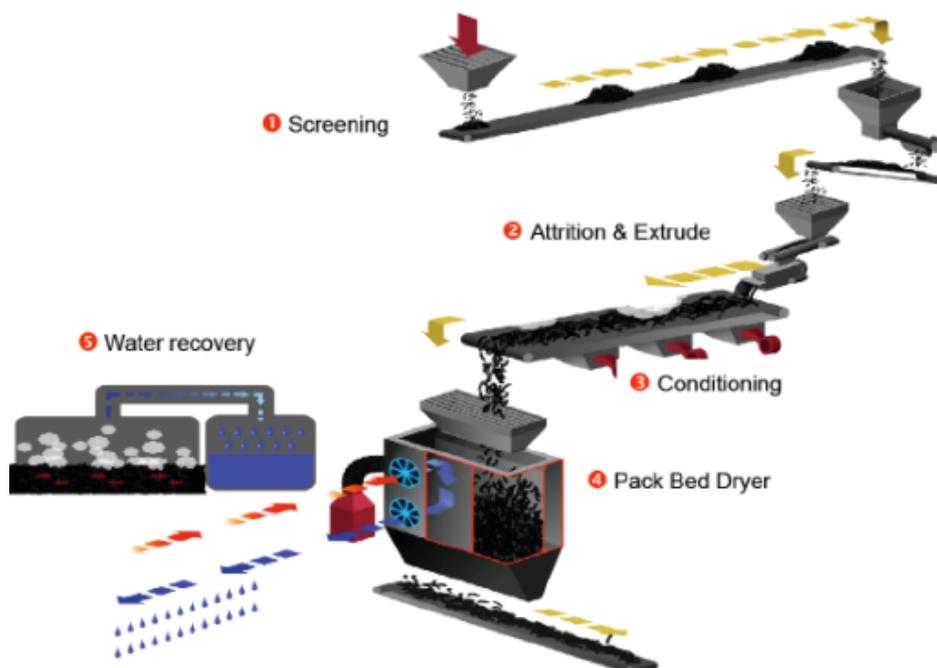


Figure 5.5: Coldry process (Godfrey 2010)

In August 2018, ECT signed a 5 year, \$1.3million supply contract with a large food manufacturer in Gippsland to supply Coldry solid fuel to support delivery of process steam via an existing solid fuel boiler system.¹⁵

ECT is currently undertaking a full feasibility program, for a proposed Coldry commercial demonstration plant at Yallourn power station in the Latrobe Valley, a project which is targeting an initial plant build of 175,000 t/y, with current scaled up potential of ~300,000 t/y.¹⁶

ECT has also developed an allied process called Matmor, in which pellets are produced from brown coal and iron oxide bearing material (e.g. iron ore, mill scale, nickel tailings) and subsequently retorted to produce iron metal (Wilson 2001). Matmor is a method of producing high-quality iron from lignite and iron oxide-bearing materials such as mill scale, nickel tailings as well as high or low grade iron ore. The iron product produced by the Matmor process is a high quality substitute for, or supplement to, scrap metal feedstock used in electric arc furnace or induction furnace. The Matmor process, described in Figure 5.6 below, represents a modification and extension to the Coldry process.

¹⁵ <http://www.ectltd.com.au/contract-signed-for-1-3-million-supply-deal-in-victoria/>

¹⁶ <http://www.ectltd.com.au/update-on-india-project-waste-to-energy-technology-acquisition-and-request-to-extend-suspension/>

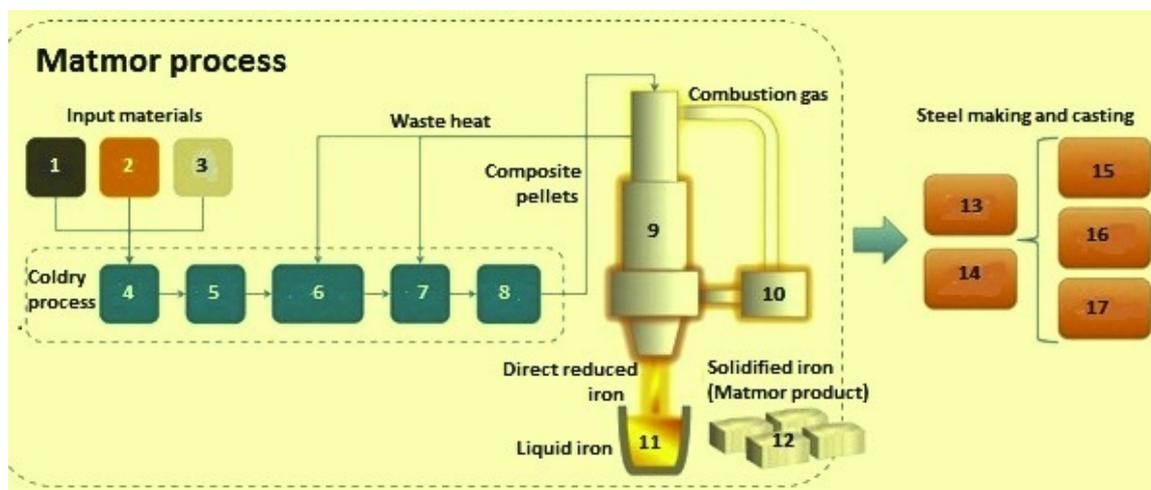


Figure 5.6: The Matmor process. Inputs: 1. Lignite, 2. Iron oxides, 3. Flux. Coldry process: 4. Feed control, 5. Attrition and extrusion, 6. Conditioning, 7. Packed bed drying, 8. Composite pellets. Iron making: 9. Matmor retort, 10. Recirculating combustion gas, 11. Liquid iron, 12. Solidified iron (Matmor product). Post Matmor processes: 13. Electric arc furnace, 14. Induction furnace, 15. Ingot casting, 16. Continuous casting, 17. Foundry.¹⁷

In the first step of the Matmor process, lignite, iron oxides and flux are ground and converted to dry pellets using the Coldry process. The composite pellets are self-reducing and self-fluxing. In the second step, the pellets are charged into the top of the Matmor retort, where they are heated in a reducing atmosphere. As the temperature of the pellets increases, the remaining moisture is evaporated and the coal volatiles are driven off as combustible gas. This combustible gas is recirculated into the base of the retort, where they are ignited, providing an effect similar to that of a blast furnace.

As the composite pellets travel down the centre of the retort, reduction reactions take place which removes oxygen from the iron oxides. The hot reduced pellets are discharged at the base of the retort. These hot pellets contain carbon, iron and ash. Hot air or oxygen is injected which burns off the remaining carbon and raises the temperature of the pellets past the melting point of the iron to produce liquid metal and slag. The liquid metal is either cast into pig iron or can be directly taken to the steel making furnace.¹⁸

In May 2018, ECT signed a memorandum of understanding to enter into a collaborative project with NMDC Limited and NLC India Limited, the largest miners of iron ore and lignite, respectively, in India, to construct a large scale integrated Coldry and Matmor pilot plant, capable of producing 2 tonnes of metal per hour.¹⁹ Completion of a formal project agreement was subject to approval by the Board of NMDC. When no such agreement had been communicated to ECT by June 2019, ECT withdrew from

¹⁷ <https://www.ispatguru.com/matmor-process-for-iron-making/>

¹⁸ <https://www.ispatguru.com/matmor-process-for-iron-making/>

¹⁹ <http://www.ectltd.com.au/historic-australia-india-rd-collaboration-agreement-signed/>

the MOU to pursue other opportunities.²⁰ These opportunities include the further development of HydroMOR (Hydrogen-based Metal Oxide Reduction), a refinement of the Matmor technology (Henley-Smith et al. 2017).

5.4 BLAST FURNACE COKE FROM LIGNITE

Globally, the production of steel increases steadily to meet the demands of a growing world population. According to the World Steel Association total production was 850 Mt in 2000²¹ and 1808 Mt in 2018.²² Production of steel relies on production of iron in blast furnaces, which in turn relies on a steady supply of coke to reduce iron oxides to metal. The coking coal used to produce coke is not abundant and relatively expensive, and is subject to frequent price fluctuations, so there is a long-standing interest in developing cheaper alternatives.

Most coals, including many bituminous coals, are not suitable for blast furnace coke production. Coking coals have the unique attribute of softening when heated, agglomerating and forming a plastic phase called mesophase. It solidifies upon cooling to form hard, strong, macroporous lumps of coke, which are chemically much less reactive than conventional coal char.

Coke is manufactured in a coke oven battery, a series of batch reactors, by carbonisation of coking coal at 1000-1200°C, generally for 18-24 h. During the carbonisation process, some of the organic compounds are converted into small volatile molecules and escape as gas. The residual coke contains about 90% carbon, in the form of small graphitic domains of high molecular weight polycyclic aromatics (Lewis 1982).



Figure 5.7: Coke for ironmaking²³

²⁰ <http://www.ectltd.com.au/shareholder-update-india-project-16/>

²¹ <https://web.archive.org/web/20150420161500/http://www.worldsteel.org/dms/internetDocumentList/statistics-archive/production-archive/steel-archive/steel-annually/steel-annually-1980-2013/document/steel%20annually%201980-2013.pdf>

²² <https://www.worldsteel.org/en/dam/jcr:dcd93336-2756-486e-aa7f-64f6be8e6b1e/2018%2520global%2520crude%2520steel%2520production.pdf>

²³ <https://www.tridge.com/intelligences/metallurgical-coke-met-coke>

Low rank coals, including lignite, have long been investigated as potential alternatives for blast furnace coke since the end of World War 2. The disadvantage of employing lignite as a coke precursor is that it does not soften on heating. However, some lignites, e.g. Victorian lignite, have a low concentration of mineral impurities (especially sulphur), which is a potential advantage during ironmaking.

In East Germany post-WW2 there was no coking coal available, so research was undertaken to develop a coke alternative from East Elbe lignite, which has low ash and sulphur content. A suitable coke substitute was produced by producing briquettes from coal dust, then carbonisation in two stages; with a slow rate of temperature rise in the first stage and faster rate in the second stage to a final temperature of 1100°C held for 20 h. Such extreme conditions resulted in high cost and low coke yield, so this process was only used until supplies of coking coal from other countries became available (Kennedy 1960).

During the 1950s and 1960s, researchers at the Gas and Fuel Corporation of Victoria attempted to produce a coke-like material from Victorian lignite. The focus of the research was to use binderless briquettes, as produced at the Yallourn briquette factory, as a precursor for carbonisation. The major problem encountered was that the briquettes cracked during carbonisation. After much trial-and-error experimentation, it was determined that the rate of temperature increase during carbonisation must be controlled to ensure that the differential shrinkage between the surface and core of the briquettes should vary as little as possible. Under optimised heating conditions it was possible to produce an acceptably strong char, but it was found to be too reactive for blast furnace use, quickly breaking down to fines (Ellis & Kennedy 1964).

In the early 1960s, FMC Corporation in the USA developed a process for producing a blast furnace coke from non-softening coals, ranging from anthracite to lignite. The distinctive feature of the FMC process was that the coal was pyrolysed and the resulting tar was processed to pitch, which was used as a binder. The pyrolysis char was calcined at about 800°C and cooled before mixing with the pitch. The mixture was briquetted and air cured before carbonisation at 900°C to obtain FMC coke (Joseph & Blake 1964). While this process transformed lignite into a material with suitable hardness characteristics, its reactivity was unacceptably high.

More recently, researchers from Kyushu University in Japan developed a process for producing a coke-like material from Indonesian lignite. Prior to hot briquetting and carbonisation, the lignite was first subjected to a combined treatment of acid washing and hydrothermal dewatering at 200°C. It was found that the acid washing removed the alkali and alkaline earth metallic species that acted to cross-link the macromolecular structure, while hydrothermal treatment rearranged the macromolecules physically. The combined treatment enhanced plasticisation and then deformation/coalescence of lignite particles, which formed high strength carbonised briquettes. However, the reactivity of the coke-like product was not determined (Mori et al. 2013).

In 2009, the Victorian Government and Japan's Kyushu Electric Power Company established a project at Monash University to investigate the production of blast furnace coke from Victorian lignite. BCIA assumed management of this project at the end of 2010. The project involved a PhD student at

Monash University, Mr Mamum Mollah, supervised by Professor Alan Chaffee, in collaboration with CSIRO, HRL Technology, and Australian Char.

Research efforts in this project were directed to production of hard, low reactivity cokes from lignite. Combinations of thermal coal treatments, binding agents and processing conditions were investigated. Briquettes were produced and tested for compressive strength and reactivity.

The research involved evaluation of a range of processing conditions, involving (1) separation of tarry material from Victorian lignite; and (2) briquetting of the mixture including the residue, a binder and a cementing agent under a carefully regulated heating regime.

Initially, Victorian lignite or pellets were impregnated with tar, pelleted at ambient temperature and carbonised. Products from Victorian lignite exhibited higher compressive strengths and slightly lower reactivity than those from briquettes, but the reactivity was much higher than that of blast furnace coke (Mollah et al. 2015).

Next, lignite and tar was hot pelleted and air cured before carbonisation. A high concentration of tar (10-15%) and air curing increased the compressive strength to higher than that of blast furnace coke, but the proportion of graphitic structure was small and the reactivity was too high (Mollah et al. 2016a).

The structure of the lignite was then altered by hydrothermal treatment and acid washing. After mixing with tar, hot pelleting and air curing the pellets were subject to severe carbonisation at 1200°C for 8 h. This combined process reduced the reactivity significantly and improved the proportion of graphitic structure, but the product still did not meet the specification for blast furnace coke (Mollah et al. 2016b).

Victorian lignite was then treated with alkali to induce melting and fusing upon carbonisation. This resulted in a slight improvement in properties, but still not to an acceptable level (Mollah et al. 2016c).

During the course of this PhD project, a set of processing conditions was identified that was successful in reducing the reactivity to close to that of blast furnace coke. The details remain confidential and the university holds a provisional patent for this material and its method of preparation.

The PhD project was completed in 2015. Since that time, further incremental improvements have been made, including the production of 50 mm briquettes (shown in Figure 5.8 below), suitable for evaluation in standard industry tests.

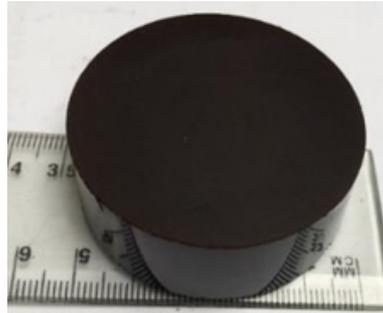


Figure 5.8: 50mm briquette produced from Victorian lignite

Monash University is seeking partners to take this development further and demonstrate it on a larger (kg) scale.

6 Activated Carbons

Activated carbon is a form of carbon that has been processed to be microporous, with a high surface area available for physical or chemical adsorption. Activated carbon has a wide diversity of applications in various fields, including the treatment of drinking water, groundwater, municipal wastewater, industrial wastewater; remediation of contaminated groundwater and soil, air and gas cleaning, solvent recovery, gas storage, and in industrial production processes such as in pharmaceuticals, chemicals, food and beverage production (Çeçen 2000).

Activated carbon is produced from carbonaceous source materials such as bamboo, coconut husk, willow peat, wood, coir, lignite, coal, and petroleum pitch. It can be produced by either physical activation or chemical activation. Physical activation involves the exposure of carbonised char to steam or CO₂ at temperatures in the range of 600–1200°C. For chemical activation, the raw material is impregnated with certain chemicals (e.g. phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, zinc chloride 25%) and then carbonised at 450–900°C. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material (Çeçen 2000).

6.1 HARD ACTIVATED CARBONS FROM VICTORIAN LIGNITE

The potential for using Victorian lignite briquettes for the manufacture of hard granular activated carbon was first investigated by Garner and Packer (1980). Crushed Yallourn briquettes were physically carbonised under steam, and the activated carbons exhibited gas-phase and liquid-phase adsorption capacities comparable to commercial products. However, the briquette-based carbons were generally too soft to be commercially competitive (Guy & Perry 1992).

Three main routes to overcome the inherent softness of Victorian brown coal for the production of hard activated carbons have been investigated, as illustrated in Figure 6.1:

1. hot briquetting to produce hard briquettes as carbonisation feedstocks;
2. the use of lignite char with a suitable binder to produce hard briquetted feedstocks for activation; and
3. chemical digestion of lignite to produce hard feedstocks in either granular or extruded form (Guy & Perry 1992).

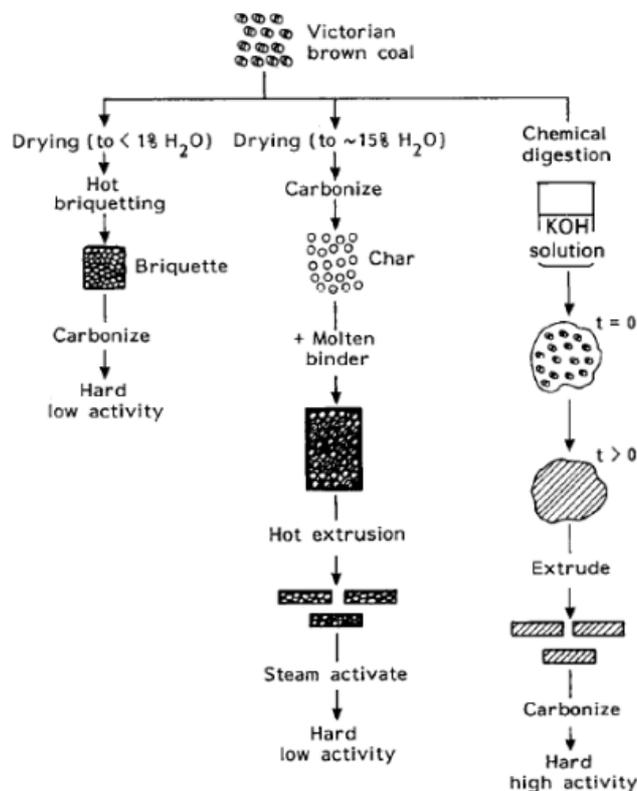


Figure 6.1: Routes for production of hard activated carbon from Victorian lignite (Guy & Perry 1992)

The main commercial target application of this research was for carbon-in-pulp (CIP) gold recovery. As part of the recovery of gold by cyanidation, activated carbon is used as an adsorbent for the aurocyanide complex. In this application, an attrition-resistant carbon is of the utmost importance, because any particle breakdown in the process leads to loss of gold.

Efforts to produce hard activated carbons via the first two routes proved to be unsuccessful, as reviewed by Guy and Perry (1992). However, the alkali digestion route introduced by Durie and Schafer (1978) proved to be more successful. The method involved digestion of the lignite with alkali to partially dissolve the coal matrix and form soluble humates, which led to the collapse of the pore structure and formation of a hard compact glassy gel on air drying. The gel was then carbonised gradually under an inert atmosphere. Varying the type of alkali and its proportion in the digestion mixture produced high surface area carbons with differing pore size distributions.

The Coal Corporation of Victoria (CCV) actively developed this process to the point where KOH-derived carbons could be consistently produced from Loy Yang lignite with high porosity and superior kinetics for adsorption of gold from solution (Verheyen et al. 1988). An example of this activated carbon product is shown in figure 6.2 below. It was demonstrated that controlled changes to the pore structure could be achieved by varying the alkali:coal ratio and the carbonisation conditions, producing activated carbons suited to different applications (Guy et al. 1990).



Figure 6.2: Hard activated carbon from Victorian lignite (courtesy V. Verheyen)

The characteristics of hard activated carbons prepared using this alkali digestion technology have been compared with those of commercial carbons used in the CIP gold recovery process. Table 6.1 compares the most significant carbon properties affecting CIP performance, indicating that the lignite-derived carbons compared favourably with commercial carbons (Guy & Perry 1992).

	Lignite-derived carbon	PICA G210 AS	Norit R3515	Norit ROW 0.8 Supra
Surface area (m ² /g)				
CO ₂ (Dubinin)	1190	1080	1160	1180
N ₂ (BET)	1130	1140	1080	1000
Micropore volume (cm ³ /g)	0.32	0.29	0.31	0.31
Total pore volume (cm ³ /g)	0.63	0.59	0.60	0.69
Iodine No. (mg/g)	1270	1180	1050	1100
Takeda hardness (%)	91	91	91	75
Stirring abrasion resistance (%)	99	100	99	-
Ash (% db)	4	2	5	7
Relative kinetic activity (h ⁻¹)	118	125	100	-
Gold capacity (kg Au/tonne C)	21	19	24	23

Table 6.1: Comparison of lignite-derived activated carbon with commercial carbons (Guy & Perry 1992)

Despite these promising results, repeated efforts to develop a commercial product proved unsuccessful. The main problem was that the market is dominated by a small number of well-established incumbents with the power to engage in a price war to prevent new entrants gaining a foothold. This problem remains true today (F. Woskoboenko, personal communication).

6.2 HONEYCOMB MONOLITH ACTIVATED CARBON FROM VICTORIAN LIGNITE

Typically, commercial activated carbons are used in the form of powders or granules, requiring the use of packed bed contactors. The purpose of such contactors is to make the pores within the carbon accessible to components of interest within a flowing stream, so that they may be adsorbed and removed from the stream. In the case of the packed beds, although the surface area per unit volume is high, there are inherent disadvantages such as high pressure drop associated with the flow through the packed media, particle entrainment and channelling. Larger particles are better than powders in such contactors, but then the large diameter can prevent full utilisation of the porosity toward the core (Gadkaree 1998).

A way to overcome this problem is to utilise an activated carbon contactor with a honeycomb structure, making use of the very high geometric surface area-to-volume ratio of this shape. The high surface area provides high contact efficiencies, with a significantly lower pressure drop. Honeycomb activated carbon monolith contactors were first developed by Kobe Steel, preparing the honeycomb structure by extrusion of a thermosetting resin such as phenol resin and then converting it to activated carbon by carbonisation at 600-1000°C (Sugino 1983). A major difficulty with this approach is that about 50 wt.% of the mass is lost during carbonisation, resulting in distortion and cracking.

To overcome this problem, Corning Inc. developed honeycomb activated carbon contactors by extrusion of a mixture of activated carbon particles and organic binder, followed by drying (DeLiso et al. 1994). Corning Inc. has a strong market position in manufacture of honeycomb ceramic filter elements for use as filters and catalytic converters to reduce gas and particulate emissions from cars and trucks.²⁴ Corning has created a portfolio of patents around honeycomb activated carbon contactors, including those comprising a thin film of activated carbon on a ceramic filter substrate. One of these patents describes the use of an electric current to heat up the carbon mass so as to allow desorption of adsorbed species, thereby regenerating the activated carbon contactor (Gadkaree & Tyndell 2000). This represents an example of an operating principle known as electrical swing adsorption (ESA).

In 2014, BCIA funded a collaborative project between Monash University and the University of Melbourne, called 'Carbon Monoliths for Capture of CO₂ by Electrical Swing Adsorption', in association with the EU-funded MATESA consortium.²⁵ The vision of MATESA is to develop a new-generation high-efficiency capture process based on selective adsorption of CO₂ on hybrid honeycomb monoliths. Part of this project, at the University of Melbourne, involved a collaboration with Corning Inc. to evaluate the performance of an activated carbon honeycomb monolith for CO₂ capture using ESA, as illustrated in Figure 6.3 below. The results of this research are embargoed until 2020 (Zhao et al. 2020).

²⁴ <https://www.corning.com/worldwide/en/innovation/materials-science/ceramics/how-it-works-filters-and-substrates.html>

²⁵ <https://www.sintef.no/projectweb/matesa/consortium>

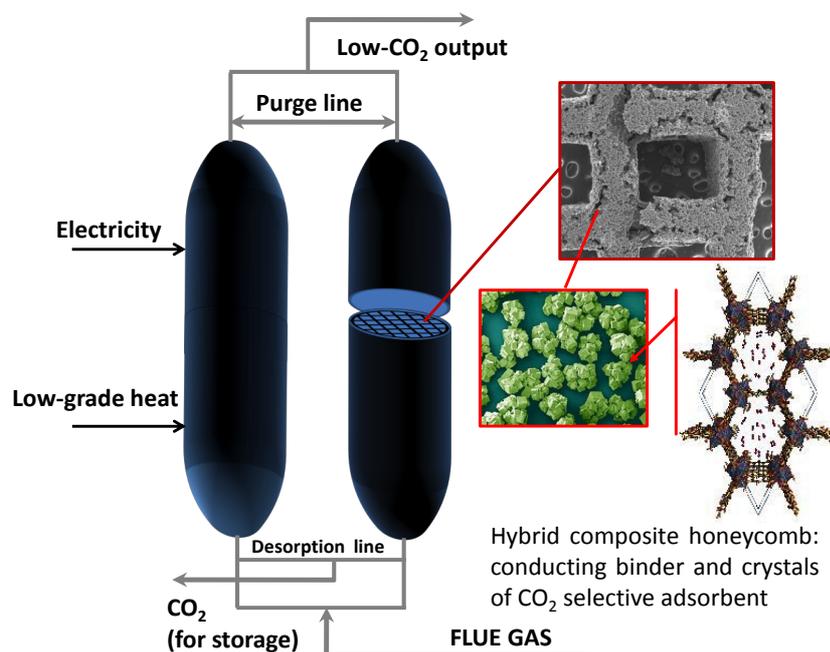


Figure 6.3: Conceptual diagram of electrical swing adsorption with honeycomb activated carbon monoliths²⁶

Another part of the project, at Monash University, involved the development of carbon monoliths based on Victorian lignite for use with ESA. Activated carbon honeycomb monoliths were produced from Victorian lignite using a similar methodology to that developed earlier for hard activated carbons. The lignite was mixed with an alkali to produce a gel material that could be extruded to form a honeycomb monolith, which was subsequently carbonised (Parsa & Chaffee 2018). The resulting activated carbon monolith is shown in Figure 6.4 below.



Figure 6.4: Honeycomb activated carbon from Victorian lignite (courtesy A. Chaffee)

²⁶ <http://www.sintef.no/projectweb/matesa/>

The activated carbon monoliths from Victorian lignite were electrically conductive, and could be heated by applying an electrical current. Attempts were made to coat the surfaces of the porous carbon with the metal organic framework UTSA-16, a high capacity CO₂ adsorbent that had been chosen by the MATESA group. However, the coatings that were prepared were not very homogeneous and they incorporated relatively low levels of UTSA-16 (<10 wt%).

Further development of the ESA concept has not continued in Victoria since the completion of this project, although the concept of ESA coupled with renewable energy has great potential as a low-cost way to scrub CO₂ from the atmosphere. Instead, the Monash University group has focussed on exploring applications for honeycomb activated carbon monoliths with greater commercial potential.

6.3 VICTORIAN RESEARCH CONTEXT

Research on activated carbon monoliths is currently under way at Monash University, led by Professor Alan Chaffee. The focus is on refining fabrication techniques for production of high quality, hard extruded product from Victorian lignite at low cost, and on development of opportunities in water treatment.

Activated carbon monoliths have potential for use in adsorption of a wide range of organic materials such as phenol, dyes, humic acid and formaldehyde, acetaldehyde and isopropanol, as well as inorganic material such as phosphorous, arsenic or other heavy metals. Additives can be incorporated into the activated carbon monoliths to increase the adsorption / oxidation of targeted contaminants. After use, the monoliths can be efficiently regenerated by applying a low voltage electric current to heat the adsorbent internally.

The products being developed at Monash University offer great potential as viable and effective industrial adsorbents for water treatment. Monash is seeking a partner to develop and commercialise this technology.²⁷

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²⁷ https://www.monash.edu/__data/assets/pdf_file/0009/1463778/Carbon-monoliths-water-purification.pdf

7 Humic Substances

7.1 COMPOSITION OF HUMIC SUBSTANCES

Humic substances are organic compounds that are important components of humus, the major organic fraction of soil, peat, and coal. They are produced by biodegradation of dead organic matter and are complex mixtures of many different organic compounds containing carboxyl and phenolate groups.

Humic substances are essential for healthy soil. They fix nitrogen, make soil nutrients available to plants through cation exchange, and improve the physical structure of the soil (Youngs & Frost 1963). Humic substances can help to reduce fertiliser application rates, enhance efficiency of nutrient use, replace synthetic plant regulators, increase water stress tolerance, decrease disease incidence, and enhance early growth and flowering, and serve as a carrier for beneficial microorganisms (Canellas et al. 2015).

It is conventional to divide humic substances into three main fractions – humic acids, fulvic acids, and humin – based on extraction in alkali. Extraction using a strongly alkali yields a solution containing humic and fulvic acids, with the humin as the insoluble residue. Humic acid is the component that is precipitated when the pH of the solution is lowered to 1, while fulvic acid is the component that remains in solution. Humic acid and fulvic acid are items of commerce, while humin is typically the waste product of manufacturing.

Humic acid is regarded as a network of aromatic rings which are joined by long-chain alkyl structures to form a flexible network. The structure contains voids of various dimensions which can trap and bind other organic components such as carbohydrates, proteins and lipids (Schulten et al. 1991). A chemical structure for the basic skeleton of humic acid is shown in Figure 7.1 below. The structure of humic acid is further complicated by the fact that individual networks and segments of networks are linked by hydrophobic bonding, with additional interactions through hydrophilic side groups.

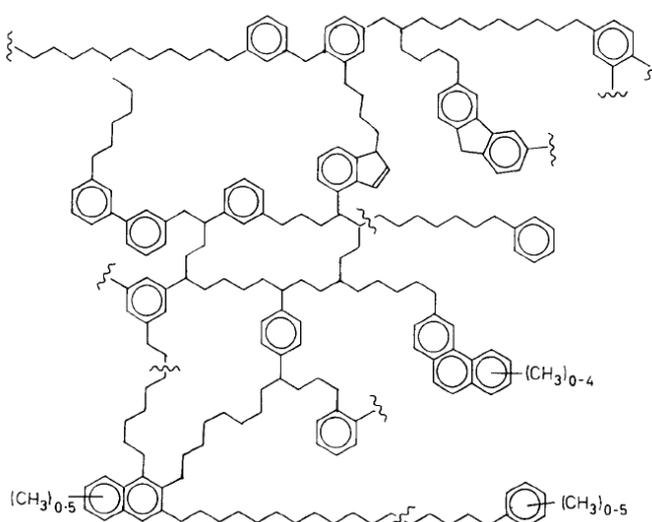


Figure 7.1: Chemical network structure of humic acid from soil (Schulten et al. 1991)

Fulvic acid is the fraction of the humic substances that is soluble at acidic and neutral pH. Fulvic acid is not a specific macromolecule, but can be visualised as a hydrophilic polymeric structure that can adsorb hydrophobic compounds. It forms a sponge-like structure made up of hydrogen-bonded phenolic and benzenecarboxylic acids, upon which alkanes and fatty acids are adsorbed. Fatty acids also form esters with phenolic humic “building blocks”. Through this mechanism, fulvic acid can fix, stabilise and preserve relatively large amounts of hydrophobic organic compounds (Schnitzer & Neyroud 1975).

7.2 AGRICULTURAL APPLICATIONS FOR HUMIC SUBSTANCES

Lignite is well known to be a beneficial soil amendment, which is readily converted into soil organic carbon. This results in improved soil structure, cation-exchange capacity and water-holding capacity, which in turn translate to increased plant yields and overall more photosynthesis and stabilisation of atmospheric CO₂ (Rumpel & Kögel-Knabner 2004; Kwiatkowska-Malina 2011; O'Halloran et al. 2011).

Humic substances extracted from lignite have found a wide range of potential applications in agriculture, including stimulation of plant growth, solubilisation of essential plant trace elements, blended with chemical fertilisers and as animal feed supplements.

7.2.1 Plant growth promotion

Humic acids are widely acknowledged as having plant growth-promoting effects, although the mechanism(s) involved are not clear. It is likely that one or more of the following factors is involved:

- Plant hormone-like effects
- Formation of chelates and improved uptake of essential micronutrients
- Decreased toxicity of aluminium and heavy metals
- Improved soil aggregation and structure
- Increased pH buffering and cation exchange capacity

As part of a research project at Monash University funded by Brown Coal Innovation Australia (BCIA), a meta-analysis was undertaken of literature reports of plant growth-promoting effects of humic substances. The goal was to determine the magnitude and likelihood of plant-growth response to exogenously-applied humic substances and to rank the factors contributing to positive growth promotion. These factors included the source of the humic substances, the environmental growing conditions, the type of plant being treated, and the manner of application. Overall, the analysis estimated that humic substance application led to shoot dry weight increases of $22 \pm 4\%$ and root dry weight increases of $21 \pm 6\%$. However, actual responses varied considerably and were mainly influenced by the source of humic substance applied, the rate of application, and to a lesser extent, plant type and growing conditions (Rose et al. 2014).

7.2.2 Chelation of metal ions

Humic substances are valued for their ability to chelate (i.e. form stable complexes) with metal ions, particularly essential plant trace elements (e.g. Fe, Mn, Zn and Cu), which would otherwise be poorly soluble. Humic substances can increase the availability of essential plant micronutrients by competitively desorbing them from insoluble complexes in the soil. Humic substances are considered to be both a source of trace elements and a carrier to transport trace elements through the soil to plant roots. For sensitive crops growing on deficient soils, the application of complexes of trace elements and humic substances can be beneficial. Fulvic acid has a lower molecular weight and a higher proportion of acidic functional groups than humic acid, so fulvic acid-metal complexes are more soluble. As such, they are highly valued and widely used in biological farming systems (Chen & Stevenson 1986).

7.2.3 Organomineral fertilisers

In China, it is well accepted that humic acid applied along with urea (a nitrogen fertiliser) can increase crop yields relative to urea-only treatments. It has been reported that 350,000 tonnes of humic acid are used in Chinese agriculture each year (Dong et al. 2009).

Similarly, the co-application of humic acid and phosphorus fertilisers can lead to increased phosphorus availability and crop yields, especially on alkaline soils. It has been demonstrated that humic acid can slow or prevent the precipitation of poorly soluble phosphates as insoluble calcium phosphates, increasing the availability of P to plants (Delgado et al. 2002; Alvarez et al. 2004).

Internationally, a number of different organomineral fertiliser products have been developed to take advantage of these properties. In Australia, Omnia Specialities produces a humic acid fertiliser coating called 'FertiCoat', which can be used with either N or P fertilisers²⁸. Extensive field trial testing has established that FertiCoat can deliver higher yields and improved fertiliser use efficiency.

7.2.4 Animal feed supplements

Research supports the benefits of humic acid for poultry growth and egg production (Yörük et al. 2004; Ozturk et al. 2010). Humic acids are also known to be beneficial for the growth of pigs (Ji et al. 2006; Wang et al. 2008) and calves (Cusack 2008).

Currently, LawrieCo in South Australia markets 'BioMAX Animal Humic Fulvic Powder' as an animal-grade mixture of humic and fulvic acids which is suitable for use with dairy, pig, poultry, cattle, sheep, horse and fish. It is said to improve feed and supplement digestion, faster animal weight gains, reduce odour in animal waste, increase dairy feed efficiency and reduce mastitis, animal stress and healing time²⁹.

²⁸ <http://www.australianhumates.com.au/product/ferticoat/>

²⁹ http://www.lawrieco.com.au/item_details.php?item_id=33&item_type=photo_gallery&content_list_id=8

7.3 COMMERCIAL PRODUCTS BASED ON HUMIC SUBSTANCES

The global market for humic substances was valued at US\$388.02 million in 2018, and it is expected to grow reach US\$624.98 million by 2028.³⁰ On the basis of crop type, the global market is segmented into row crops, fruits and vegetables, turf and ornamentals, and others. Humic substances are being used in a variety of concentrations and physical forms for usage in these applications, either directly by spraying, or by adding them to soil.

The vast majority of commercially-available humic substances are extracted from naturally oxidised lignite, which is called “leonardite” after A. G. Leonard, early director of the North Dakota Geological Survey, who did much of the early work on oxidised lignite outcrops in North Dakota. Oxidation of lignite breaks down the humin component, allowing more humic acid to be extracted. North Dakota leonardite contains up to 86wt% humic acid (dry, ash-free basis) (Youngs & Frost 1963).

Commercial products containing leonardite, humic acid and fulvic acid are currently produced by many companies around the world. Table 7.1 below provides an (incomplete) overview of the range of products available.

Company	Country	Products/Trademarks
Actagro	USA	Actagro Liquid Humus
Adler Agro	Spain	Humic acid
Agrofill	Italy	Humic acid
Agxplore International	USA	HA12
Apg Tarim	Turkey	Leonardite, humic acid, fulvic acid, K-humate
Arvensis	Spain	Humipower
Biolchim	Italy	Take Up, Humidrip, Humic Up
Borregard Lignotech	USA	Borregro line
Brandt Consolidated	USA	Uptake, Leonardite Plus
Canadian Humalite International	Canada	Liquid and power extracts from oxidised sub-bituminous coal
CIFO	Italy	Biotron line, Cifoumic
Cosmolcel	Mexico	Humical, Humicrop, H-85
Double Dragons Humic Acid Co	China	Humic acid, K-humate, P-humate, B-humate, Nitro humic acid, Poultry Mate
Fine Humate Industry Co	China	Humic acid, Na-humate, K-humate, NH ₄ -humate
GOFAR Agro Specialities	China	Fulvic acid, humic acid, Na-humate, K-humate
Greenworks Technology	China	Huminova – Leonardite, humus, K-humate, B-humate, fulvic acid
Hazem Kimya	Turkey	Flash-OTD (Leonardite)
Hefe Fertilizer	Spain	Hefe Humus
Helena Chemicals	USA	Hydra-Hume, Trafos
Humic Growth Solutions	USA	Humi-K line, Ful-Gro

³⁰ <https://www.globenewswire.com/news-release/2019/04/08/1799138/0/en/Humic-Acid-Market-To-Reach-USD-624-98-Million-By-2026-Reports-And-Data.html>

Humintech	Germany	Liqhumus, Powhumus, Perlhumus
Jiloca Industrial	Spain	Humilig, Fulvin
Liaoyang County Decavem Import and Export	China	Decavem line (humic acid, fulvic acid, Na-humate, K-humate, nitro humic acid)
Live Earth	USA	Granular humate range, Great-8, Liquid-6
Loadstar Unimars	Latvia	Na-humate
Mapon Humic Acid Development	China	Humistrong
Numerator Technologies	USA	NuHumic WDG Verge
Omnia Specialities	Australia/ South Africa	K-humate, K-fulvate, fulvic acid
Quimica Foliar	Mexico	Acidos Fulvicos, Fulvigran, QF Activator
Shandong Chuangxin Humic Acid Technology	China	Humic acid, fulvic acid, K-humate, fulvic + urea
Shenyang Humate Technology	China	Huminrich
SNLO	Romania	Ferthum, Folhum (K-humate organomineral fertilisers)
SPA-Ret	Russia	Lignohumate
Timac Agro	Spain	Fertiactyl GZ (sulfonated humates)
Tradecorp International	Spain	Humical, Humistar
Valagro	Italy	Fulvic 100, Humic 80, AU15%
Vellsam Materias Bioactivas	Spain	Humivel line
VM Crop Care	India	Biostar, Humic Acid, Leonardite soil conditioner
Xi'an Tbio Crop Science	China	Humic acid, fulvic acid, K-humate

Table 7.1: Commercially available humic substances produced from lignite

Germany-based Humintech GmbH is a major player in the humic acid market. With a consumer base in almost 70 countries, the company has been ranked as the leading technology company for humic acid based products, which are produced from German lignite.³¹

In Australia, the Coal Corporation of Victoria developed a process for extracting humic acid from Victorian lignite. The process was licensed to HRL Agriculture, which was subsequently purchased by the Omnia group of South Africa. Omnia Specialities (Australia) Pty Ltd currently sells both liquid and dried forms of humic substances to the local and international markets.³²

Omnia Specialities produces humic acid and fulvic acid in Morwell from a naturally oxidised fraction of Victorian lignite, which is a particularly rich natural source of humates. Omnia Specialities has recently invested in a multimillion dollar upgrade of its manufacturing plant, shown in Figure 7.2 below, making it a key production facility for export of these lignite-sourced products around the globe.

³¹ *Ibid.*

³² <https://www.omnia.com.au>



Figure 7.2: Omnia Specialities manufacturing plant, Morwell

7.4 VICTORIAN RESEARCH CONTEXT

Omnia Specialities is currently collaborating with the Carbon Technology Research Centre at Federation University in a project funded by ACI and ANLEC R&D, to investigate improvements in the production of humic substances from lignite.

The aim of the project is to develop and refine a lab-scale oxidation process to tailor the preparation of humic and fulvic acids in high yield, regardless of lignite source. The overall goal of the project is to develop a tailored lignite oxidation process that will offer better ability to vary the reaction conditions, increase yields and achieve more desirable properties of the produced humic substances.

This project is intended to assist Omnia Specialities by developing an improved humate extraction approach, to increase the humate content in run-of-mine lignite and boost the capacity of the manufacturing facility in Morwell.

This collaboration between Federation University and Omnia Specialities, supported by funding from ACI, has the potential to increase export revenue from the Latrobe Valley and create opportunities for more widespread use of humic substances in Australian agriculture.

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8 Carbon Fibres

8.1 INTRODUCTION TO CARBON FIBRES

Carbon fibres contain at least 92 wt% carbon and have diameters of about 5–10 μm . They are made of anisotropic carbon, meaning that the carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fibre. Carbon fibres generally have excellent tensile properties, low densities, high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance (Huang 2009).

For practical use, several thousand carbon fibres are bundled together to form a tow, which may be used by itself or formed into woven textiles, prepregs, continuous fibres/rovings, and chopped fibres. Composite parts can be produced through filament winding, tape winding, pultrusion, compression moulding, vacuum bagging, liquid moulding, and injection moulding (Huang 2009). Carbon fibre composites provide a lightweight material with excellent structural properties, and find use in aircraft, automobiles, boats, machine parts, high-grade sporting goods, pressure vessels, wind turbine blades, civil engineering, and so on (Liu & Kumar 2012).

Figure 8.1 below shows a micrograph of a carbon fibre about 5–7 μm in diameter, a cloth woven from carbon fibres, and a golf club fabricated from carbon fibre composite.



Figure 8.1: Micrograph of individual carbon fibre³³; woven carbon fibre cloth; golf club fabricated with carbon fibre composite³⁴

Carbon fibres can be further processed and transformed into a wide range of value-added products. Figure 8.2 below illustrates the diversity of products produced from KRECA pitch-based carbon fibres by Kureha Corporation in Japan. In addition to being woven into fibre cloth, carbon fibres can be chopped and milled to lengths ranging from 0.1 mm to several millimetres. The chopped material can be compounded with suitable polymers and used in disk brake pads, gaskets for gas sealing, seal rings and packings. The chopped material can also be formed into nonwoven flexible felt or rigid

³³ https://web-japan.org/trends/11_sci-tech/sci120329_2.html

³⁴ <http://www.golfalot.com/equipment-reviews/taylormade-m1-driver-review-3340.aspx>

insulating components, for use as insulation in high temperature furnaces, e.g., furnaces to manufacture silicon ingots for solar cells or semiconductors.³⁵

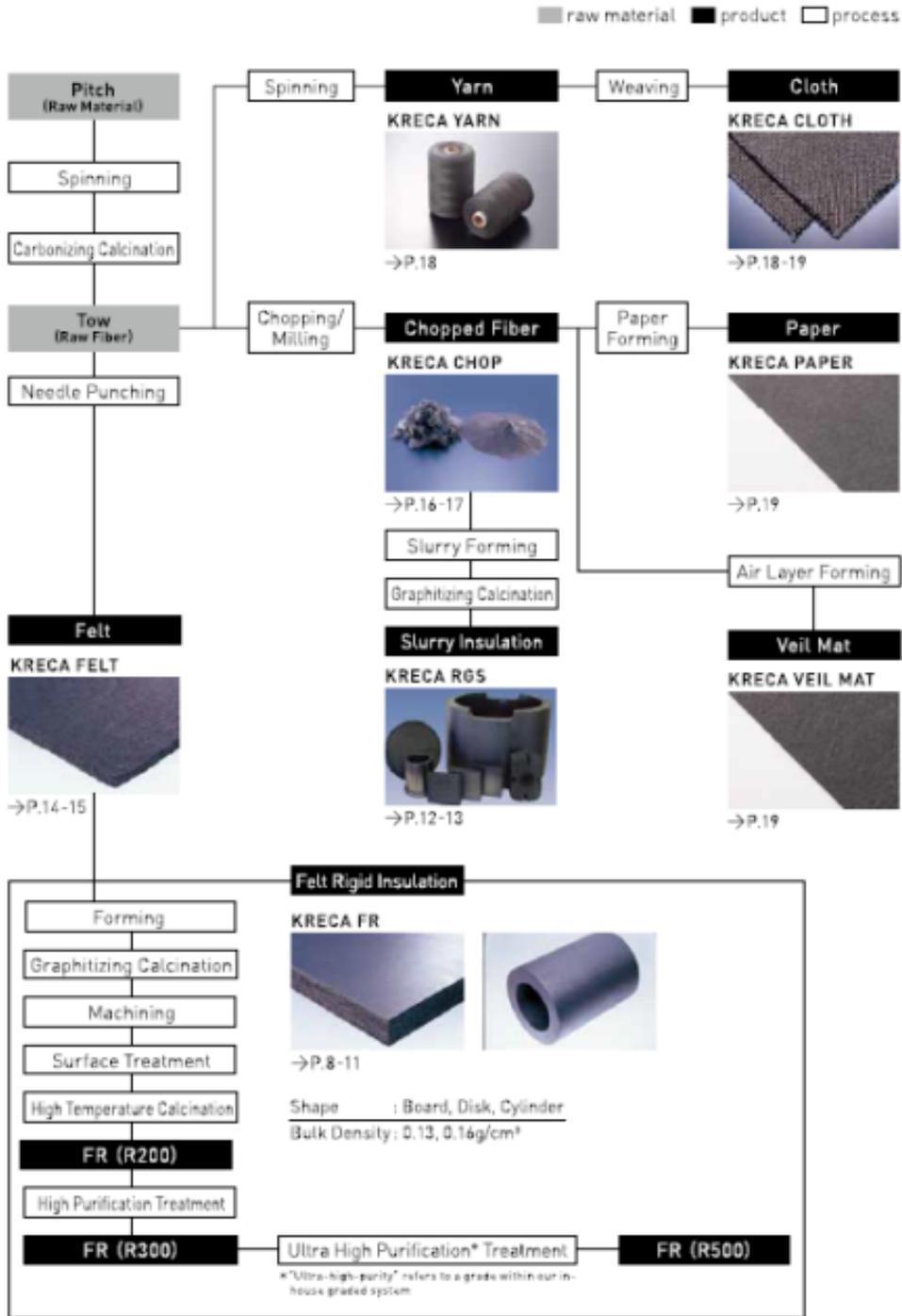


Figure 8.2: Value-added products from KRECA pitch-based carbon fibres³⁶

³⁵ <https://www.kureha.co.jp/en/business/material/kureca.html>

³⁶ https://www.kureha.co.jp/en/business/material/pdf/KRECA_eng.pdf

The global carbon fibre market reached \$1.98B in 2014, while the carbon fibre composite market (including all matrix materials) reached \$16.6B in 2014. Forecasts predict the carbon fibre and carbon fibre composite markets will grow to \$4.3B and \$33.6B in 2021, respectively, driven largely by growth in the continually expanding aerospace and industrial markets. Global carbon fibre demand is expected to increase from 58,000 tonnes in 2015 to greater than 100,000 tonnes by 2020 (Newcomb 2016).

As shown in Figure 8.3 below, manufacturers Toray (Zoltek), SGL, Mitsubishi Chemical Carbon Fiber and Composites, Toho Tenax (Teijin), Formosa Plastics Corporation, Hexcel and Solvay (Cytec) comprise nearly 80% of the carbon fibre market. Pitch-based carbon fibres are manufactured by MCCFC, Cytec and Nippon Graphite Fiber (Frank et al. 2012).

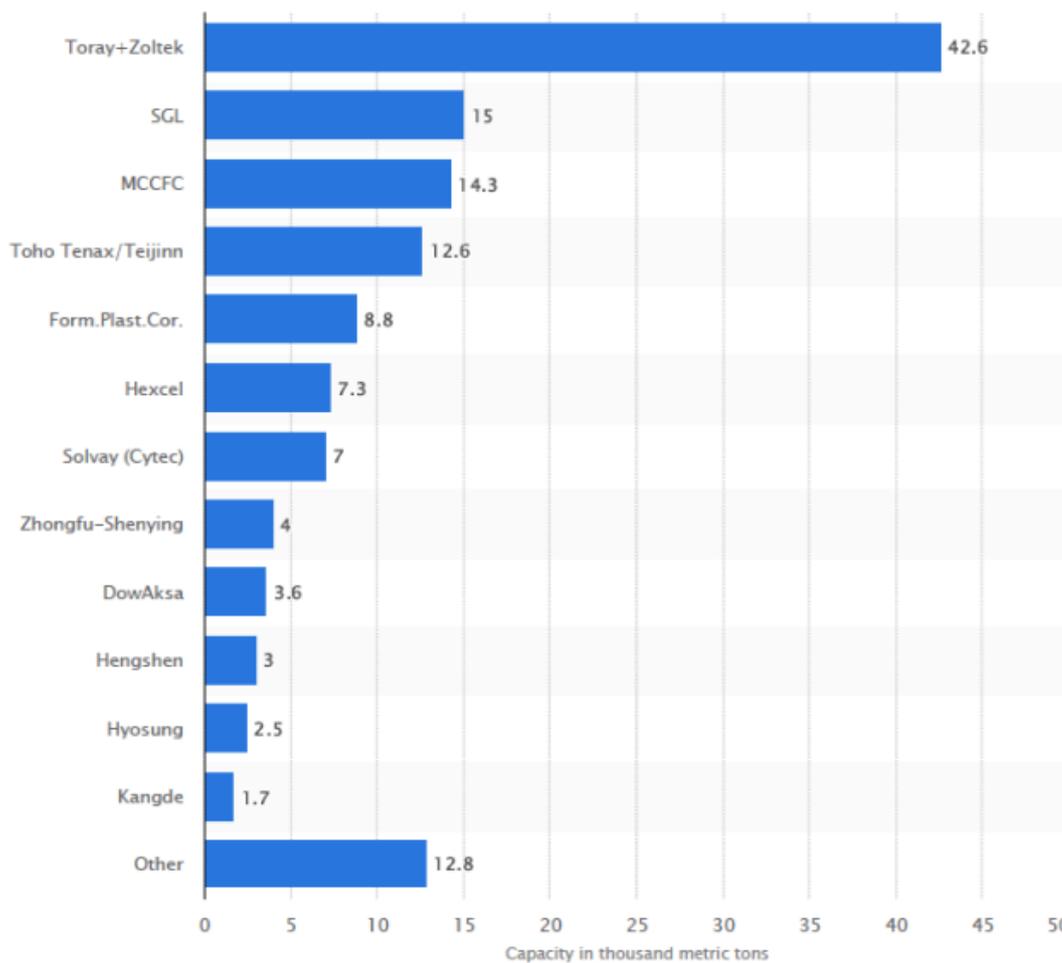


Figure 8.3: Leading carbon fibre manufacturers by production capacity in 2017 (in 1,000 tonnes)³⁷

³⁷ <https://www.statista.com/statistics/380543/production-capacity-of-top-carbon-fiber-manufacturers/>

8.2 TYPES OF CARBON FIBRES

Applications of carbon fibres as reinforcement material began in the 1960s, wherein synthetic rayon (from cellulose) was used as the precursor. In the early 1960s, polyacrylonitrile (PAN) fibres were found to produce carbon fibres with higher tensile and compressive strength than rayon based carbon fibres. Subsequently, petroleum pitch was used to make high modulus carbon fibres (Liu & Kumar 2012). Currently, PAN serves as the principal precursor (~96% of the carbon fibre market) material for carbon fibre production, and the rest are made from pitch. Rayon has no commercial importance today as a precursor for carbon fibres (Newcomb 2016).

Three main types of carbon fibre are produced: general purpose grade, high performance grade and activated carbon fibres. Activated carbon fibres are produced from general purpose grade carbon fibres, and are discussed further in Section 8.6 below. General purpose and high performance grades of carbon fibre are differentiated on the basis of their tensile modulus and tensile strength, as illustrated in Figure 8.4 below.

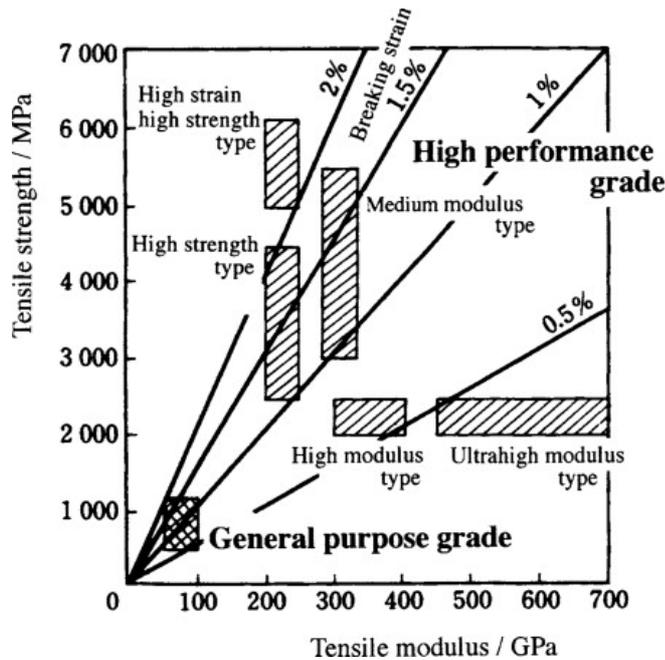


Figure 8.4: Classification of carbon fibre types by mechanical property (Inagaki 2000)

Different precursor materials are used to produce the various types of carbon fibre, as illustrated in Figure 8.5 below.

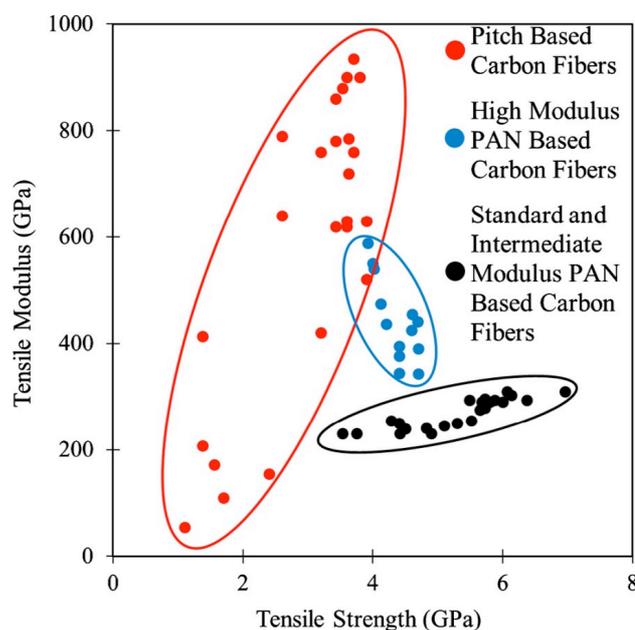


Figure 8.5: Tensile modulus plotted against tensile strength for commercially available pitch and PAN based carbon fibres (Newcomb 2016)

The range of mechanical properties available for each of the three commercial types of carbon fibre are summarised in Table 8.1 below.

	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at breakage (%)
PAN-based	3.5 – 6.8	170 - 650	1.3 – 2.4
Mesophase pitch-based	2.2 – 3.5	140 - 820	0.2 – 1.1
Isotropic pitch-based	0.5 – 1.0	30 - 40	1.4 – 2.4

Table 8.1: Mechanical properties of commercial carbon fibres (Kim et al. 2016).

There are significant differences in the cost of these different types of carbon fibre. Comparative cost data is scarce in the public domain, but a very dated direct comparison was provided by Edie (1990), as shown in Table 8.2 below.

	Cost of	Cost of Carbon
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	Precursor (US\$/kg)	Fibre (US\$/kg)
PAN-based	0.40	60.00
Mesophase pitch-based	0.25	90.00
Isotropic pitch-based	0.25	22.00

Table 8.2: Relative cost of PAN-, mesophase- and isotropic-based carbon fibres (Edie 1990)

For comparison, the current cost for PAN-based carbon fibres is in the US\$15-20/kg range (Gill et al. 2017), and presumably the cost of pitch-based fibres would have fallen in the intervening period as well.

8.3 MELT-SPUN PITCH-BASED CARBON FIBRES

As indicated in Table 1, pitch is a cheap raw material for carbon fibre production. Pitch from petroleum or coal tar has a high carbon content (>80%) and is rich in asphaltenes, which consist of large, alkylated, plate-like molecules of condensed aromatic rings. The pitch from petroleum and coal tar is isotropic, and needs only to be distilled and filtered prior to being melt spun directly into isotropic pitch fibres. These carbon fibres exhibit a relatively low molecular orientation and a higher concentration of defects and flaws, resulting in lower tensile strength and tensile modulus (Edie 1990).

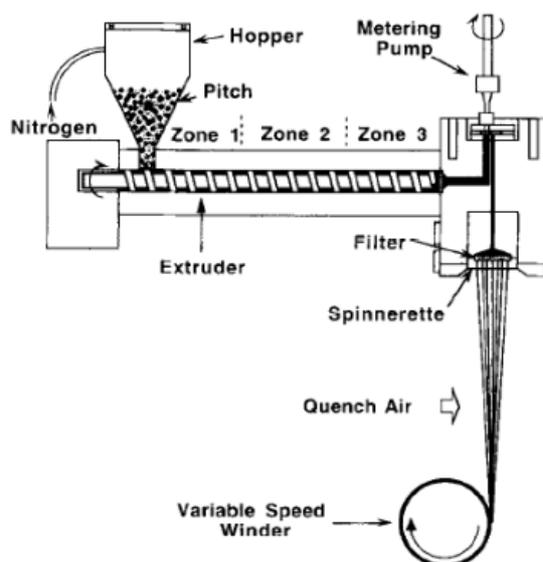


Figure 8.6: Melt-spinning process to produce pitch-based carbon fibres (Edie 1998)

Low cost isotropic pitch-based carbon fibres are used in general purpose, non-structural applications where high strength and stiffness are not required, such as filters, static dissipation, electromagnetic interference shielding, thermal insulation, brake and clutch frictional materials, carbon fibre reinforced concrete, and as a replacement for asbestos in some insulation and roofing material applications (Eddie 1990).

To produce high performance grade carbon fibres, such as are used in aerospace applications, it is necessary for the carbon to have a graphitic structure oriented along the fibre axis. To accomplish this, prior to melt spinning, the pitch precursor must be extensively heat treated to convert it to an oriented, anisotropic liquid known as mesophase pitch. Under heat treatment, the aromatic carbon in the pitch condenses to form small spherical particles (mesophase spheres) which are composed of stacked polynuclear aromatic hydrocarbon molecules (shown in Figure 8.7 below). Upon further heating or catalytic polymerization, the concentration of the mesophase spheres increases, causing them to collide, coalesce and align, forming a mosaic-like nematic liquid crystal structure. This facilitates the development of excellent molecular orientation during the melt spinning process. The graphitic structure of mesophase fibres results in higher elastic modulus and higher thermal and electrical conductivity along the fibre direction (Eddie 1990).

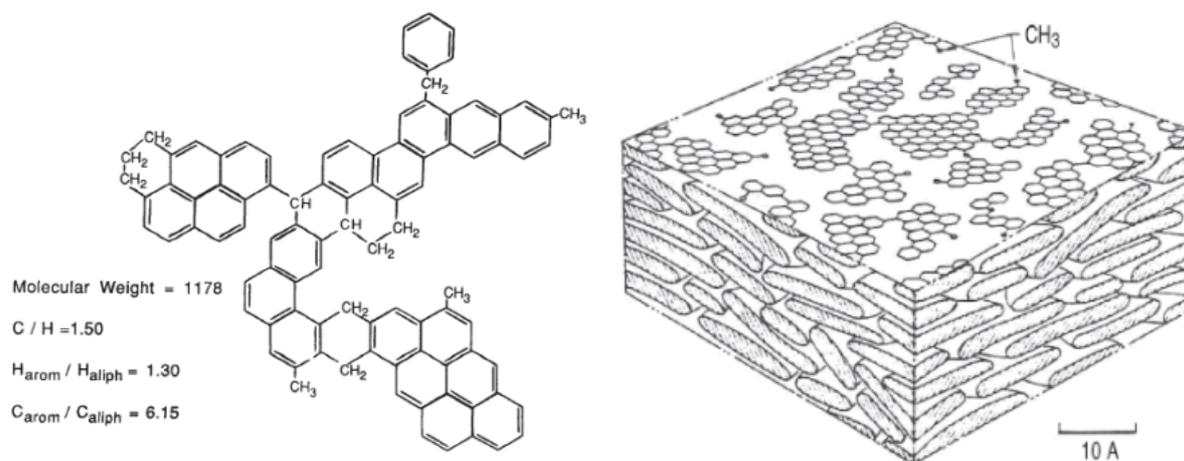


Figure 8.7: Models of mesophase structure (Eddie 1990) and lamellar liquid crystal phase (Minus & Kumar 2005)

Production of mesophase carbon fibres is highly specialised, and is only undertaken by three companies (Mitsubishi Chemical Carbon Fiber and Composites, Cytec and Nippon Graphite Fiber). Each stage of the process (pitch purification, mesophase formation, and fibre spinning) is proprietary and has been optimised by in-house research, leading to their significantly higher cost (Eddie 1990).

Presently, because of their superior stiffness, mesophase fibers are used in aerospace structural applications. Because of their extremely high thermal conductivity, they are also used for dissipating heat in high speed machinery and in electronic packages (Park & Heo 2015).

8.4 WET-SPUN PAN-BASED CARBON FIBRES

PAN-based carbon fibres can be tailored for use in a broad range of intermediate applications. PAN-based polymers are the optimum precursors for the carbon fibres owing to a combination of tensile and compressive properties as well as the carbon yield. Unlike pitch, PAN-based polymers cannot be processed using conventional melt-spinning techniques, as they undergo a thermally induced cyclization reaction below their melting points. Instead, they are produced by the more expensive wet spinning method, with PAN dissolved in a solvent 'dope' (Frank et al. 2014).

The conventional wet-spinning technique, illustrated in Figure 8.8 below, entails extrusion of the copolymer solution into a precipitation bath, where jets of the spinning dope leaving the spinneret come into contact with substances miscible with the solvent but which do not dissolve the polymer.

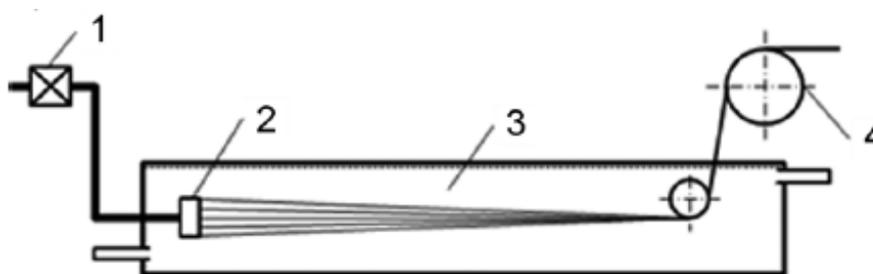


Figure 8.8: Wet spinning technique; 1: metering pump, 2: spinneret, 3: precipitation bath, 4: take-up godet (Frank et al. 2014)

The polymer solution is spun through a spinneret with multiple holes, a total of 100–500000, each having a diameter in the range 40–100 μm . The solvent is directly extracted from the polymer solution into the coagulation bath, where diffusion-controlled phase transitions play a determining role. The most important issue is to obtain fibres with the optimum morphological structure, which is very sensitive to the composition and conditions within the coagulation bath (Frank et al. 2014).

The wet spinning process used for PAN-based carbon fibres is more expensive than the melt spinning technique used for pitch. It has been necessary to take this approach because PAN goes through a thermally induced cyclisation reaction below its melting point, making melt spinning impossible unless large amounts of solvent and plasticiser are added. Wet spinning is more costly than melt spinning due to the relatively low spinning speed and longer processing time. On the other hand, melt spinning is a more difficult process, due to its high sensitivity to rheological properties and the need for close process control of each step of the process (Choi et al. 2019).

The advantage of PAN, and the reason that it has not yet been supplanted by cheaper replacements, is that its molecular structure converts during heat processing to a dense, well-ordered aromatic structure, producing very high quality carbon fibres. Generally, the heat treatment of PAN-based precursor fibres involves three steps, i.e., oxidation, carbonization, and graphitization, as shown in Figure 8.9 below.

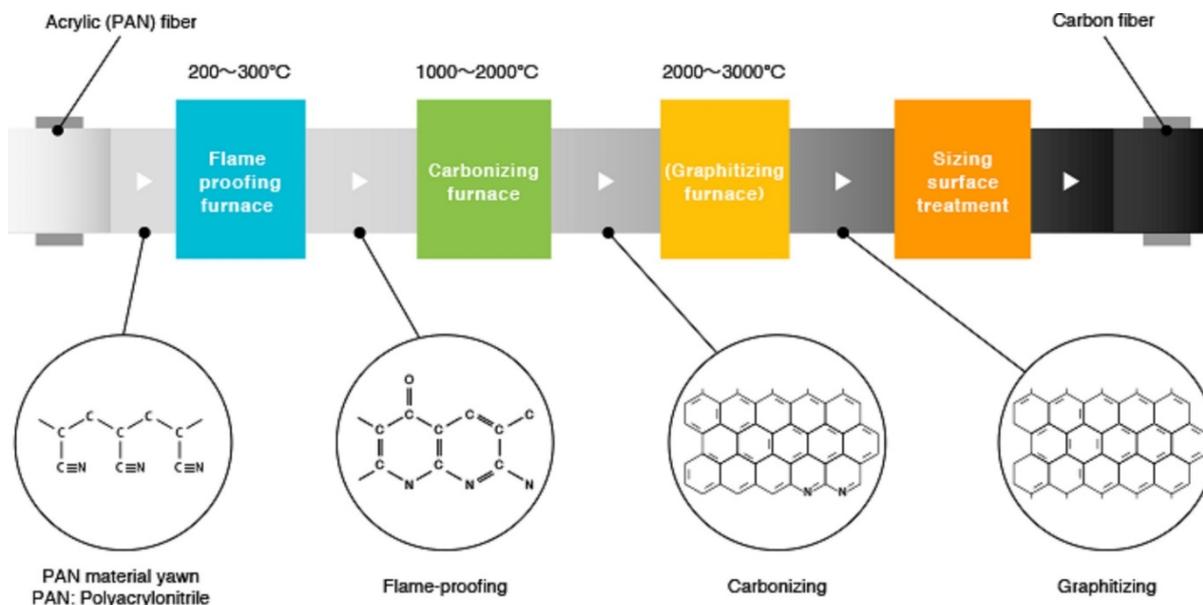


Figure 8.9: Chemical conversion during production of PAN-based carbon fibres³⁸

The precursor fibre is first oxidised at a temperature between 200 and 300°C, which results in the formation of N-containing ladder-type polymers. This allows further processing at higher temperatures. After oxidation, the fibres are carbonised at temperatures up to 1200–1600°C in an inert atmosphere to obtain a turbostratic carbon structure. Then, to improve the ordering and orientation of the basal planes in the direction of the fibre axis, the fibre can be graphitised at up to 3000°C, depending upon the required tensile modulus (Frank et al. 2014).

The surface of commercial carbon fibres is modified to increase inter-laminar shear strength between the carbon fibres and the resin matrix so load can be effectively transferred from the fibres to the matrix in a composite. The common surface treatment methods include oxidation (gas-phase, liquid-phase, and catalytic), non-oxidation (deposition of active carbons and grafting), and plasma treatment. In addition, a sizing agent can be applied on the carbon fibre surface to improve fibre processability and interfacial properties with matrix. (Liu & Kumar 2012).

The transformation from PAN precursor fibre to finished carbon fibre is illustrated in Figure 8.10 below.

³⁸ <https://www.doylesails.com/innovation/about-stratis/carbon-technora/carbon>

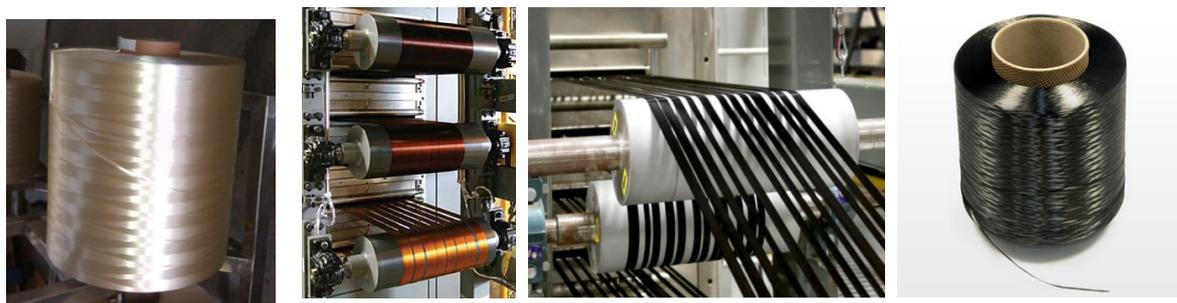


Figure 8.10: Stages in the production of PAN-based carbon fibre; (i) PAN precursor fibre; (ii) oxidation; (iii) carbonisation; (iv) finished carbon fibre.

While the majority of carbon fibres produced commercially are based on PAN, the high cost of the PAN precursor fibre has been a restricting factor. With conventional processing using a carbon fibre-grade PAN, precursor is over 50% of the carbon fibre cost (Baker & Rials 2013).

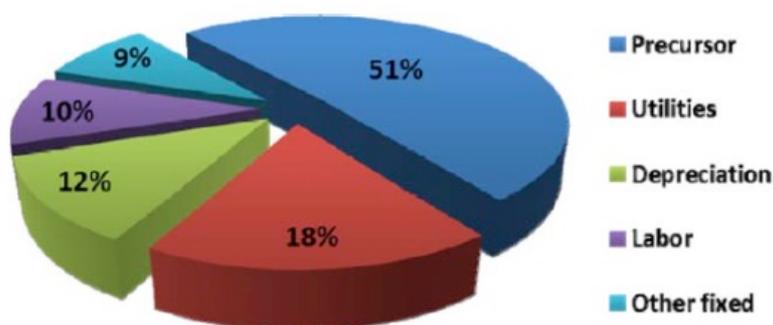


Figure 8.11: Breakdown of cost elements in the manufacture of carbon fibre from PAN (Baker & Rials 2013).

The high volume automotive industry is a very attractive target market, where fibre reinforced polymeric composites offer reduced weight and superior styling. PAN-based carbon fibre could offer as much as 60% weight reduction, but at (at current prices) up to ten times the cost (Baker & Rials 2013). In 2009, a US DOE-funded program specified that carbon fibres suitable for the automotive industry should have tensile strength of > 1.72 GPa, tensile modulus of > 172 GPa, elongation at break of > 1.0%, at a cost of US\$11.00-15.40/kg (Warren 2011).

Reference to Table 8.1 above reveals that there is currently no commercial carbon fibre available to meet this specification. The large commercial opportunity represented by the automotive industry market has stimulated intense research activity to meet the DOE target specifications.

8.5 ELECTROSPUN CARBON FIBRES

Electrospinning is currently the only technique that allows the fabrication of continuous fibres with diameters down to a few nanometres. Fibres with complex architectures, such as core-shell fibres or hollow fibres, can be produced by special electrospinning methods. It is also possible to produce structures ranging from single fibres to ordered arrangements of fibres.

In a typical electrospinning experiment in a laboratory, a polymer solution or melt is pumped through a thin nozzle with an inner diameter on the order of 100 μm (Figure 8.12). The nozzle simultaneously serves as an electrode, to which a high electric field of 100–500 kV/m is applied, and the distance to the counter electrode is 10–25 cm in laboratory systems. The applied voltage causes a cone-shaped deformation of the drop of polymer solution. On the way to the counter electrode, the charged liquid jet can elongate into a single fibre of considerable length with an extremely small diameter.

Electrospun nanofibers down to diameters of a few nanometres have been observed (Figure 8.13).

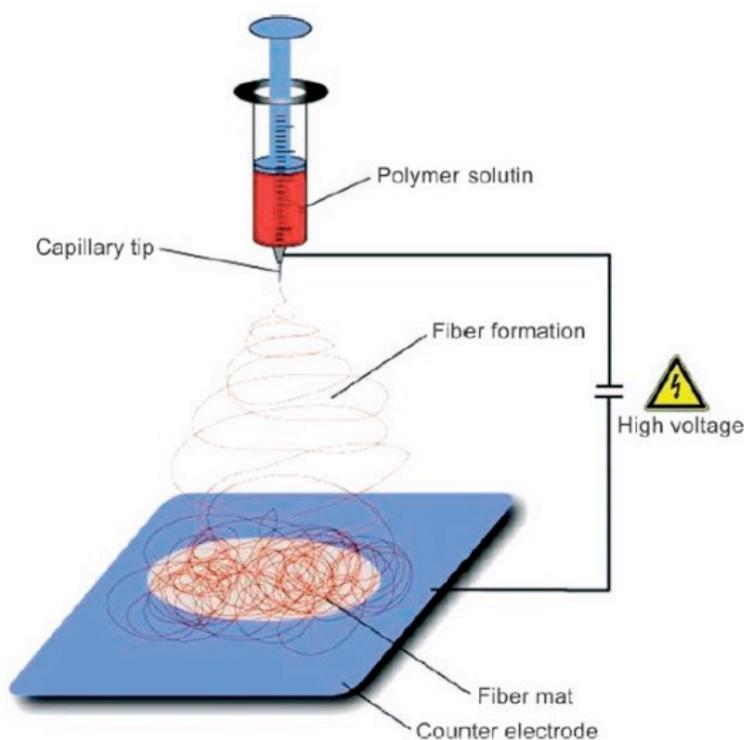


Figure 8.12: Laboratory electrospinning setup (Greiner & Wendorff 2007)

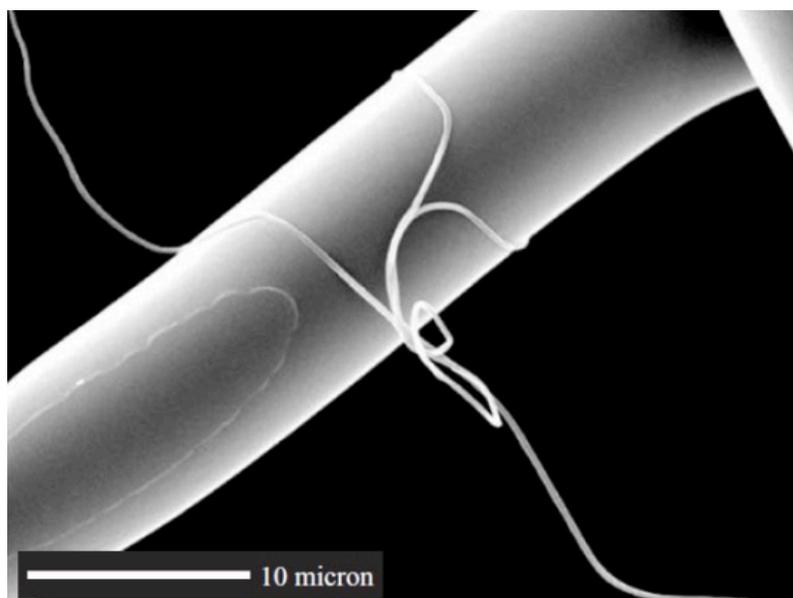


Figure 8.13: Size comparison of electrospun and conventionally spun polypropylene fibres. The diameter of the electrospun fibre is approximately 300 nm (Burger et al. 2006)

Electrospinning is commonly used as a laboratory technique to check the potential spinnability of precursor blends by wet-spinning. However, electrospun polymers are also used for applications in their own right, such as for use in combination with conventional textiles (for example, as interlinings) to increase the wind resistance, to regulate the water-vapour permeability, for improved thermal insulation, or to give the textile a specific functionality (such as aerosol filtering or protection against chemical or biological hazards). Nanofibres are already used extensively in air filters, and are being developed as catalyst supports and for medical applications such as tissue scaffolds, wound dressings and drug carriers (Greiner & Wendorff 2007).

Carbon nanofibres can be produced from nanofiber precursors by stabilisation and carbonisation, but in the form of a nonwoven mat rather than a fibre tow. Carbon nanofibres are mechanically weak, so their applications are based on their superior physical properties such as high specific surface area, high electrical conductivity and good biocompatibility. Applications for electrospun carbon nanofibres that capitalise on these properties include electrodes for lithium-ion batteries, as supercapacitors, in solar cells and sensors, for catalysis, as adsorbents, and for tissue regeneration (Zhang et al. 2014).

8.6 ACTIVATED CARBON FIBRES

Activated carbon fibres (ACFs) are porous carbons, usually prepared from general-purpose carbon fibres, having a well-defined porous structure with high adsorption capacity. ACFs have unique characteristics compared with granular or powder activated carbons. Their thin fibre shape allows more efficient mass transfer, allowing them to achieve high adsorption capacity in a smaller volume. This makes ACFs very useful for applications such as water purification, heavy metal removal, SO₂

and NOx removal, biomedical applications, capacitors, vapour sensing, refrigeration, catalysis, electrochemical applications, natural gas and biogas storage (Lee et al. 2014).

Commercial ACFs were first produced from viscose cloth precursors in 1966 (Suzuki 1994). Global ACF production was 5,580 tonnes in 2017, worth US\$344.3 million. The value of this market is anticipated to rise to US\$530 million by the end of 2025.³⁹

The main characteristics and advantages of ACFs are:

- (a) extremely high surface area (around 2000 m²/g) and correspondingly high adsorption capacity;
- (b) Fine and uniform diameter of fibre shape, which essentially eliminates limitation of mass transfer and allows rapid rates of adsorption and desorption;
- (c) Narrow and uniform pore size distribution, typically in the order of 0.8 – 1 nm; and
- (d) Ability to be fabricated in a variety of formats i.e., woven cloths, nonwoven mats, papers and felts (Lee et al. 2014).

Activation of carbon fibres involves the selective removal of carbon, generally as carbon monoxide, to generate a porous microstructure. An increased degree of activation, or 'carbon burn-off', produces a larger surface area through a broader micropore size distribution and enhanced total micropore volume. A common technique for the activation of carbon fibres is heat treatment at temperatures between 650°C and 900°C in an atmosphere of carbon dioxide or steam. Generally, the use of steam produces lower microporosity volumes than carbon dioxide (Osmond 2000).

The method and degree of activation influences the physical properties of the resultant ACF. For example, activation of pitch fibres by carbon dioxide causes the fibres to expand and swell, deforming the external layers. Conversely, steam activation causes shrinkage of the fibre diameter. Generally, increased activation yields a decreased surface density, an increased flexibility and a corresponding reduction in tensile strength (Osmond 2000).

The adsorption characteristics of activated carbon can be directly influenced by surface functional groups which derive from the composition of the precursor and the production (carbonisation/activation) process. Further modification can be achieved by nitrogenation, chlorination and oxidation treatments. The surface of the carbon fibre can also be impregnated with transition metal salts to allow the adsorption of various vapours through chemisorption (Osmond 2000).

The application of a polymer coating to ACF has produced materials that control the transfer of water and oxygen across the cloth barrier and inhibit micro-organism passage. Applications for ACF that adsorb micro-organisms include particulate filtration, wound dressings, bandages for large discharge ulcers, odour controls in hospitals, medical personnel masks and in blood purification (Osmond 2000).

³⁹ <https://www.globenewswire.com/news-release/2019/01/10/1686042/0/en/Global-Activated-Carbon-Fiber-ACF-Market-to-US-530-Mn-by-end-of-2025-QY-Research-Inc.html>

8.7 STRATEGIES TO REDUCE THE COST OF CARBON FIBRES

The automotive industry is an attractive target market for carbon fibre manufacturers, because of the high volumes that would be required. However, cost is the major barrier to entry into this market, so intensive research efforts have been made to either improve the performance characteristics of low-cost pitch-based fibres or to reduce the cost of PAN-based carbon fibres. Strategies that have been explored to reduce the cost of PAN-based fibres include melt-spinning of PAN and use of cheaper precursor materials, such as textile-grade PAN fibres, lignin or lignite. A brief description of progress made with these strategies is provided below.

8.7.1 Improvements to pitch-based carbon fibres

Raw pitches from coal tar and petroleum residues are heterogeneous with relatively low molecular weights and do not have all the desired bulk properties (e.g., softening points above 200°C, high solubility, high carbon yield and easily oxidisable) for making carbon fibres.

Recently, Kim et al. (2013) reported a thermal bromination/ dehydrobromination method to prepare high performance pitch with an appropriate softening point. The introduction of bromine to 2-methylnaphthalene induced intermolecular cross-linking of aromatic hydrocarbons through dehydrogenation polycondensation, producing a pitch consisting of linear methylene chains of polycondensed aromatic molecules. The obtained pitch was a suitable precursor for electrospinning and melt-spinning to prepare carbon nanofibers and carbon fibres, respectively.

This process was subsequently used to treat naphtha-cracked oil (NCO), resulting in a linear, isotropically oriented pitch. Carbon fibres produced from this pitch exhibited a tensile strength of 1.50 GPa and elongation at break of 3.2%.

The improved properties were attributed to the bridging of aromatic groups by methylene alkyl chains, creating a linear structure that became aligned under flow conditions (shown in Figure 8.14 below). This relatively flexible structure is quite different from the molecular structures of usual spinnable mesophase pitches (Kim et al. 2014).

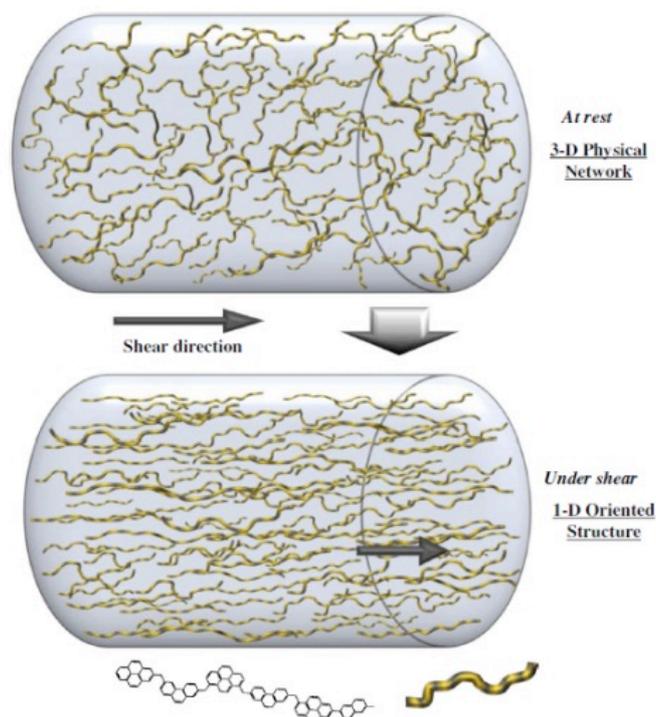


Figure 8.14: Shear-induced orientation of brominated/dehydrobrominated isotropic pitch (Kim et al. 2014).

This research group went on to produce an improved isotropic pitch was synthesised by bromination/dehydrobromination of a mixture of NCO and coal tar pitch. Fibres produced from this pitch were carbonised at 800°C for 5 min, producing carbon fibres with tensile strength of 1.8GPa and elongation of 3.2% (Kim et al. 2016). Most recently, Liu et al. (2019) demonstrated the production of carbon fibres by bromination/dehydrobromination of a 1:2 ratio of pyrolysed fuel oil and coal tar pitch. The carbon fibres exhibited a tensile strength of 1.7 GPa, modulus of 1.06 GPa and elongation of 1.6%.

These developments indicate that use of the bromination/dehydrobromination reaction has the potential to allow production of automotive-grade carbon fibres from isotropic pitch in the near future. At this stage it is unclear how cost-effective this will be.

8.7.2 Melt-spinning of PAN-based carbon fibres

As mentioned above, melt-spinning of PAN is not possible because it goes through a thermally induced cyclisation reaction below its melting point. One approach that has been tried to overcome this problem is to introduce additives to the dope mixture to reduce the interactions between nitrile groups of the polymer chain and lower the melting point. Grove et al. (1988) produced melt-spun PAN fibres using water as a plasticiser to lower the viscosity and the melting point of PAN. The carbon fibres had a tensile strength of 2.5 GPa and tensile modulus of 173-214 GPa, but had significant surface defects and internal voids. Min et al. (1992) found that supercooling of the PAN/water mixture

resulted in a defect-free fibre surface, but the internal volume was microporous. There seems to have been no further developments in this line of enquiry.

Another approach that has been pursued is to develop solvent-free PAN copolymers for melt-spinning. Some moderately successful attempts are reviewed in Choi et al. (2019). A more successful recent example is provided by Lee et al. (2019), in which PAN copolymers containing varying amounts of methyl acrylate (MA). The rheological properties of P(AN-co-MA) with MA content of 15 mol% at 190°C proved to be suitable for melt-spinning. In order to prevent remelting and fusion of the fibres in the stabilisation process, electron-beam irradiation of 1500 kGy was used. The produced carbon fibres were found to be smooth and defect-free. The melt-spun P(AN-co-MA) exhibited a tensile strength of 1.37 ± 0.2 GPa, tensile modulus of 110 ± 11.1 GPa, and elongation at break of $1.27 \pm 0.28\%$. These values are currently the highest for PAN carbon fibres produced by melt processing (Lee et al. 2019).

These results demonstrate that progress is being made in producing PAN-based fibres by melt-spinning, although it seems doubtful that this alone will be sufficient to reduce the production cost to the level needed for the automotive industry.

8.7.3 Lower cost alternatives to PAN

High-strength CFs used in current structural composite applications are almost exclusively derived from PAN precursor fibres. The evolution of toxic by-products accompanied by the fact that a large amount of organic solvent is needed during the coagulation step, the production of PAN-based carbon fibre is not an environment-friendly procedure (Ogale et al. 2019).

8.7.3.1 Low cost polymers

Textile-grade PAN fibres are commonly used in the production of blankets, carpets, and clothes. The product unit cost of textile-grade PAN fibres is low because of the high volume of production. It is speculated that the carbon fibre production cost could be reduced by up to 39% by adopting low-cost textile PAN fibres as a precursor. Textile-grade PAN fibres are not readily processed, and are not suitable for carbon fibre production due to uncontrollable oxidation or an extremely long time for stabilisation. Prior to the traditional oxidation and carbonisation processes, a chemical treatment is required to render the textile grade PAN suitable for further processing (Choi et al. 2019).

Since the early 2000s, Oak Ridge National Laboratory (ORNL) researchers have studied textile-grade PAN as a pathway to lower-cost carbon fibres, and have developed a plasma oxidation process to replace thermal ovens to oxidise or stabilise the precursor fibres. A plasma oxidation system has been demonstrated to be much faster and use significantly less energy while making a fibre with better qualities. The plasma oxidation process generates a highly reactive gas from the air that reacts with PAN much faster than molecular oxygen, reducing the processing time to less than 30 min and using 75% less energy (Choi et al. 2019). The resultant carbon fibres exhibited tensile strength of 1.72-2.96 GPa and modulus of 136-235 GPa (Paulauskas et al. 2009). ORNL has been able to manufacture carbon fibre from a textile grade precursor, provided by Kaltex, with a tensile strength as

high as 3.4 GPa (Sloan & Black 2015). Such results show great promise, and ORNL is seeking to license this technology for commercial development (Newcomb 2016).

Adopting a similar approach, Yoo et al. (2017) applied electron-beam irradiation to textile-grade PAN fibres prior to thermal stabilisation to fabricate carbon fibres. In the absence of irradiation, textile-grade PAN fibres undergo superficial fusion between filaments during thermal stabilisation, due to a high content of co-monomers. However, electron-beam irradiation prior to thermal stabilisation prevented the superficial fusion, and reduced the total stabilisation time by 64%. The elongation of irradiated fibres was suppressed and the glass transition temperature shifted to higher temperatures. The carbon fibres produced exhibited a tensile strength of 1.83 ± 0.23 GPa, tensile modulus of 147.44 ± 4.55 GPa and elongation-to-failure of $1.30 \pm 0.15\%$.

Based on these results, textile-grade PAN precursor fibres show promise as an alternative low-cost precursor to reduce the production cost of carbon fibres with commercially-acceptable mechanical properties.

8.7.3.2 Lignin

Due to the large quantities of waste lignin created during papermaking, lignin has been extensively investigated as a raw material for carbon fibre fabrication. It is not intended to provide a comprehensive review of this topic, as existing reviews are available elsewhere, e.g., Baker & Rials (2013), Frank et al. (2014), Chatterjee & Saito (2015), Ogale et al. (2016), Al Aiti et al. (2018), Souto et al. (2018), Choi et al. (2019). Instead, the intention is to provide a broad overview and to highlight the significant developments.

Generally speaking, the fibre spinning processes that are in current commercial use can be classified into three main types: (i) melt-spinning, (ii) wet-spinning, and (iii) dry-spinning. Lignin has been evaluated as a feedstock in each of these processes, as can be seen from the selected summary provided in Table 8.3 below.

Precursor	Spinning method	Tensile strength (GPa)	Tensile Modulus (GPa)	Elongation (%)	Notes	Reference
Hardwood Kraft lignin	Dry	0.79	-	-		Otani et al. 1969
Steam-exploded hardwood lignin	Melt	0.53	50	1.07	Phenolation of lignin	Sudo & Shimizu 1994
Organosolv hardwood lignin	Melt	0.355 ± 0.53	39.1 ± 13.3	0.98 ± 0.25		Uraki et al. 1995
Hardwood Kraft lignin	Melt	0.52 ± 0.18	28.6 ± 3.2	-	Lignin purified with organic solvents	Baker et al. 2012
Softwood lignin plus hardwood	Melt	~0.3	~30	0.7 – 1.2	Lignin purified by LignoBoost	Nordström et al 2013

lignin ultrafiltration permeate					process	
Blends of switchgrass and yellow poplar lignins	Melt	0.23 – 0.75	30 - 40	1.07 – 1.41		Hosseinaei et al. 2017
Hardwood Kraft lignin/PEO	Melt	0.30 – 0.55	30 - 60	0.6 – 1.5	Lignin was deashed/ devolatilised 3% PEO	Kadla et al. 2002
Hardwood Kraft lignin/PET	Melt	0.7	94	1.06	25% PET	Kubo & Kadla 2005
Calcium lignosulfonate/ acrylonitrile/ itaconic acid	Wet	1.74 ± 0.20	210 ± 6.1	0.93 ± 0.10	20% lignosulfonate	Liu et al. 2018
Bamboo tar resin	Melt	0.632	44	-	Polymerised with formaldehyde, oxalic acid & HCl catalysts	Qiao et al. 2005
Bio Pitch Liquefied wood (Chinese fir)	Melt	1.22 - 1.7	114 - 176	3.0 - 4.7	Acid solution curing HCHO and HCl at 95°C for 4h	Xiaojun & Guangjie 2010
Hardwood pyrolytic lignin	Melt	0.855 ± 0.159	85 ± 37	1.01 ± 0.3	Pyrolysis oil washed with toluene	Qu et al. 2016
Lignin/PAN	Wet	1.68	201	0.76	65% PAN	Husman 2012
Softwood craft lignin & softwood Kraft fibre	Wet	1.07	76	-		Bengtsson et al. 2019
Softwood Kraft lignin	Dry	1.07	52	2	Acetylation	Zhang & Ogale 2014

Table 8.3: Representative examples of carbon fibres from low-cost precursors

Over the past 50 years, a range of strategies have been investigated to improve the mechanical properties of lignin-based carbon fibres, including purification and fractionation of lignins, use of lignin

blends, chemical modification of lignin, and blending with various polymers. Despite all these efforts, there has not been a great deal of improvement in lignin-based carbon fibre properties. However, most of these studies were carried out on a small scale, producing small quantities of single filament lignin fibres that were subsequently stabilised and carbonised. The fibres obtained were typically of greater than 30 μm in diameter and exhibited many flaws (Baker et al. 2012), and tended to be brittle and fragile. Such results did not necessarily reflect the mechanical properties that could be achieved at industrial scale, with optimised control of fibre spinning, stretching and heating rates.

To address this shortfall, between 2001 and 2012, the US Department of Energy funded the Oak Ridge National Laboratory (ORNL) to establish a pilot-scale melt-spinning carbon fibre production line, and to investigate the potential of lignins provided by industrial partners: Organosolv lignin (Lignol Innovations), softwood Kraft lignin (Kruger Wayagamack) and LignoBoost softwood and hardwood lignin fractions (Innventia) (Baker 2010). It was demonstrated that satisfactory melt-spun carbon fibres could be produced under optimised conditions from selected purified lignins and combinations of lignin fractions, but the mechanical properties remained poor. This led to consideration of the use of blends of lignin and polymers to improve the mechanical properties (Baker et al. 2012).

One of the significant outcomes of this project was the empirical development of a set of lignin purity specifications for successful melt-spinning: purity > 99%; volatile content <5% at 250°C; ash content < 1000 ppm; < 500 ppm of particulate matter with diameter > 1 μm ; and carbohydrate residual < 500 ppm. There is currently no specification for the allowable sulphur content in lignin, although its presence favours the formation of voids and defects during carbonisation (Souto et al. 2018).

During the period of the ORNL project, researchers at the US timber products company, Weyerhaeuser, took out a patent for a process for wet-spinning carbon fibres from PAN and up to 45wt% lignin (Bissett & Herriott 2014). In 2011, Weyerhaeuser entered into a partnership with carbon fibre manufacturer Zoltek to develop the technology with DOE funding until 2014, which included installation of a wet-spinning carbon fibre pilot plant at Zoltek. The best reported result was with a lignin loading of 35wt%, producing a carbon fibre with tensile strength of 1.68GPa, tensile modulus of 201 GPa and elongation to break of 0.76% (Husman 2012), which came close to meeting the DOE automotive industry targets for mechanical properties. Further improvements could presumably be made using a more refined form of lignin.

However, a major problem with this approach was that the lignin and PAN did not form a synergistic blend. Lignin only acted as a heterogeneous filler, with the strength of the carbon fibre deriving entirely from the PAN component. With increasing lignin content, unacceptable macro-voids were formed in the fibres. Production problems were experienced because some lignin leached out of the fibres in the coagulation bath (Husman 2012).

Since then, efforts have been made to improve the spinning and blending properties of lignin through chemical modification, by esterification or alkylation. For example, Chatterjee et al. (2014a, 2014b) used different acid anhydrides to react with lignin and found that the esterified lignins were highly compatible with melt-extrusion processing for preparation of fibres. However, the esterified lignin

fibers were difficult to stabilise because the unreactive ester groups would not cross-link during thermal oxidation. Zhang & Ogale (2014) obtained better results using a partially acetylated lignin and a dry-spinning technique to prepare carbon fibers with tensile modulus of 52 GPa and tensile strength of up to 1.0 GPa. Ding et al. (2016) demonstrated that butyration of lignin made it more compatible with PAN, resulting in improved mechanical properties.

A collaborative research team in China further addressed the issue of mutual incompatibility by preparing a copolymer of esterified liginosulfonate (LS) and acrylonitrile (AN), which was successfully wet-spun to produce LS-AN carbon fibres with dense structure and free of macro-voids (Ouyang et al. 2017). The same team then obtained improved properties by incorporating itaconic acid (AC) to form a liginosulfonate-acrylonitrile-itaconic acid (LS-AN-IA) terpolymer, producing carbon fibres containing 20% liginosulfonate with tensile strength of 1.74 GPa, tensile modulus of 210 GPa, and elongation of 0.93% (Liu et al. 2018). This performance comes very close to achieving the DOE target for the automotive industry.

8.7.3.3 Lignite

Lignite is produced by the humification of plant material, which involves the biodegradation of the cellulosic components and partial degradation of the carboxyl, carbonyl and methoxy functional groups associated with lignin (Salmon et al. 2009). Structurally, it is very similar to lignin, as shown in Figure 8.15 below.

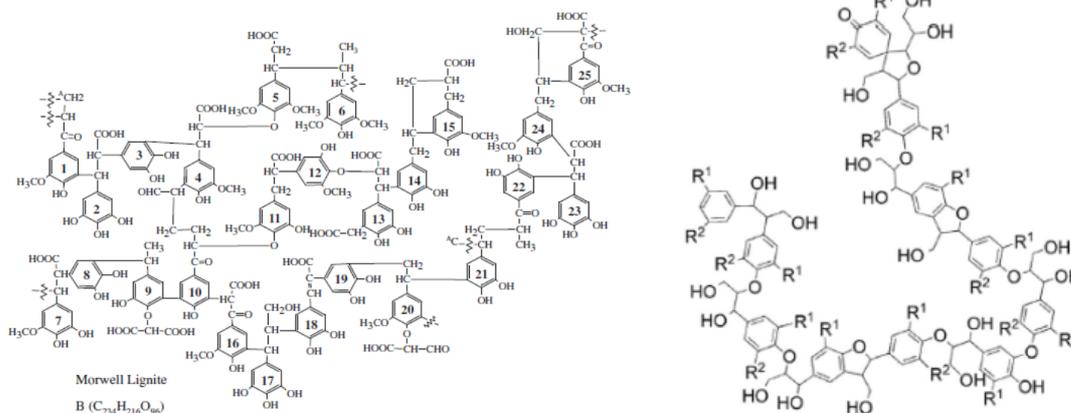


Figure 8.15: Structural models of (a) Morwell lignite (Salmon et al. 2009) and (b) lignin (Choi et al. 2019)

In principle, there are several reasons why lignite (and Victorian lignite in particular) could be an attractive source of low-cost carbon fibre precursor material. Firstly, Victorian lignite is a highly pure carbon source containing only 1-4 wt% mineral matter, which is mainly present as ionically-bound cationic species (e.g. Na, Ca, Mg, Fe) that can be removed by acid leaching. In comparison, technical Kraft lignins contain covalently-bound sulphur up to 3 wt% which cannot be removed with further purification (Frank et al. 2014).

Secondly, Victorian lignite is abundant and cheaply mined. There is an economic reserve of 33 billion tonnes with a very shallow layer of overburden. In comparison, the vast majority of Kraft lignin is burned for heat needed for drying in papermaking operations, so high quality purified lignin is in short supply.

However, comparatively little work has been done to investigate the production of carbon fibres from lignite, and most of that has been done in the context of melt-spinning. However, this work is also relevant to wet-spinning, as it demonstrates that suitable precursor materials can be extracted from lignite by a variety of methods.

For example, Oyabu et al. (1982) produced a carbon fibre feedstock heating pulverised Victorian lignite in a suitable solvent (e.g. middle tar oil), under 5.9 MPa hydrogen pressure at 300-500°C. The resultant solution was subject to filtration and then vacuum distillation to recover the solvent. The obtained 'solvent refined coal' had an insoluble content of 0.1-0.3%, and could be melt-spun to produce carbon fibres of 10-15 µm diameter and tensile strength of ~1.3 GPa.

Researchers at the CSIRO Division of Coal Technology achieved promising results using vacuum bottoms from the products of Victorian lignite hydrogenation to produce a mesophase pitch as a carbon fibre precursor. However, no results from this work were published (Allardice & Newell 1991).

Li et al. (2017) produced a carbon fibre precursor from Loy Yang lignite by extraction with 1-methylnaphthalene at 350°C. The extract had an ash content of 0.3%. The melt-spun carbon fibres, illustrated in Figure 8.16 below, were isotropic with diameter of 4-6 µm in diameter. The mechanical properties of the carbon fibres were not determined.

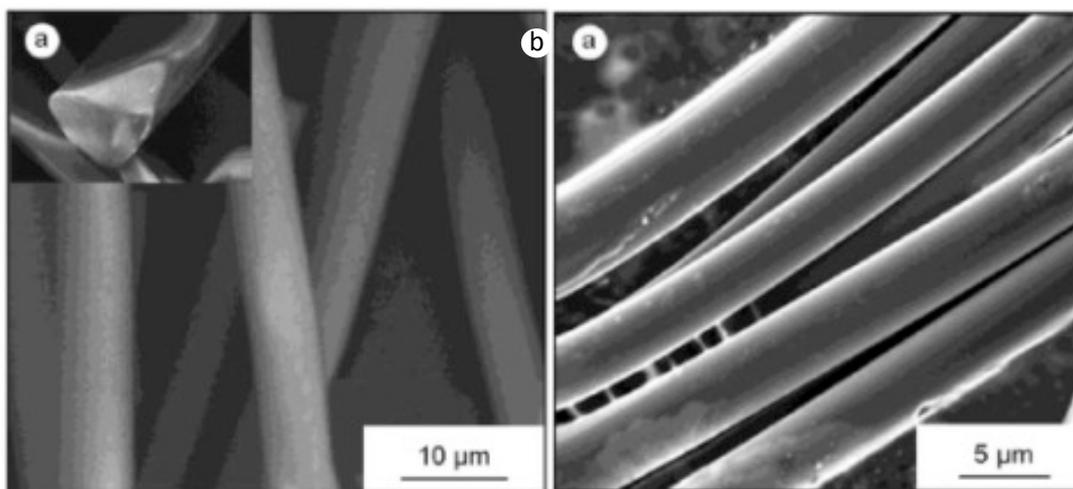


Figure 8.16: SEM images of (a) precursor fibres and (b) carbon fibres melt-spun from a solvent extract of Loy Yang lignite (Li et al. 2017)

Zhao et al. (2016) successfully produced carbon nanofibers by electrospinning a mixture of lignite-derived humic acid and PAN. Agricultural-grade humic acid was used, after purification to remove salts and mineral contaminants. The resulting fibre mat was carbonised and evaluated as an electrode for lithium ion batteries. A carbon nanofiber produced from a mixture of 30% humic acid and 70% PAN, carbonised at 800°C, shown in Figure 8.17 below, was found to produce the best results.

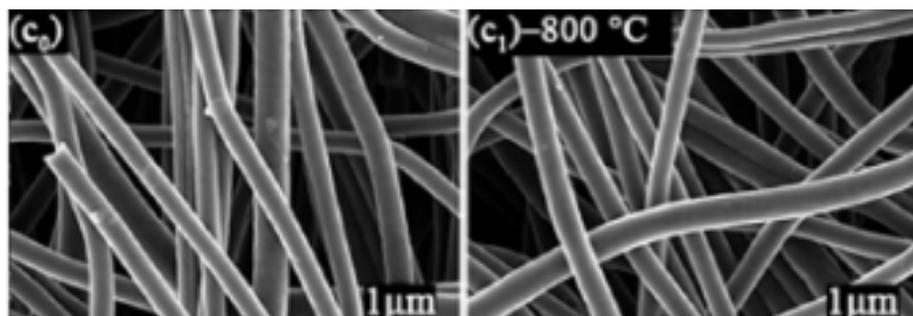


Figure 8.17: Precursor and 800°C carbonised nanofibers produced from humic acid and PAN (Zhao et al. 2016)

Likewise, Zhao et al. (2014) also produced electrospun fibres from a blend of PAN and humic acid, extracted from bituminous coal. The resulting mat of fibres was subsequently converted to activated carbon. Similarly, Guo et al. (2015) produced electrospun fibres from a blend of polyvinyl alcohol (PVA) and humic acid extracted from bituminous coal. The resulting porous carbon fibres were evaluated as supercapacitor electrodes.

These results are very promising, and suggest that there is scope to produce high quality carbon fibres from precursors extracted from lignite. The structural similarities between lignite and lignin suggest that the hard-won lessons learned from efforts to fabricate carbon fibres from lignin will also be applicable to lignite. The abundance and low cost of lignite provide motivation to transform it into an economically competitive carbon fibre precursor.

8.8 VICTORIAN RESEARCH CONTEXT

ACI and ANLEC R&D are currently funding a collaborative project between Monash and Deakin universities, investigating the possibility of producing a low cost precursor derived from Victorian lignite as a substitute for expensive PAN in carbon fibres.

The 12 month project brings together two unique Victorian research capabilities. The team at the School of Chemistry at Monash University, led by Professor Alan Chaffee, has expertise in chemical transformation and fractionation of Victorian lignite. The team at Carbon Nexus at Deakin University, led by Associate Professor Minoo Naebe, has expertise in production and characterisation of carbon fibres and their composites.

This first-of-its-kind project is aimed at proof-of-concept, laboratory-scale preparation of carbon fibres from Victorian lignite with characteristics appropriate to specific applications. The team at Monash University are preparing a range of materials from Victorian lignite by different techniques, while the Deakin University team at Carbon Nexus are looking at transforming these precursor materials into raw fibres and subsequent conversion into carbon fibre.

This project is positioned to take advantage of the potential synergies between the low cost lignite resource in the Latrobe Valley and Carbon Nexus, located at Deakin University’s Geelong Warrn Ponds Campus. Carbon Nexus is a globally unique carbon fibre and composite materials research facility, which houses an industrial pilot and research scale carbon fibre processing line, a precursor fibre spinning line and composite manufacturing capabilities. Both a research scale line and a pilot line capable of producing between 20 and 100 tonnes of fibre per year, shown in Figure 8.18 below, are capable of converting a range of precursors to carbon fibre.



Figure 8.18: Pilot and research carbon fibre lines at Carbon Nexus

The Carbon Nexus research facility is located at the heart of a growing carbon fibre and composites manufacturing precinct. Local companies include Carbon Revolution, which manufactures carbon fibre wheels for the global automotive industry, and Quickstep, which manufactures carbon fibre composite materials for the aerospace/defence industries. Carbon Nexus is thus ideally placed to engage with the full spectrum of manufacturing industries, from aerospace and automotive to defence, medical and beyond. With its range of research and production equipment, the facility enables the scientific development of new and novel carbon fibre products. It also has the resources to take these concepts from the laboratory to the production phase.

This project will identify suitable market opportunities for carbon fibres produced from Victorian lignite, and develop strategies for industry engagement to facilitate further research development.

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9 Graphene-based Products

9.1 GRAPHENE

9.1.1 Graphene overview

Graphene is the name given to a two-dimensional monolayer sheet of sp^2 -hybridized carbon arranged in a honeycomb network, representing a single layer of a graphite structure. The molecular structure of graphene (see Figure 9.1 below) is the basic structural element of other allotropes, including carbon nanotubes, fullerenes and graphene quantum dots. Graphene is the only form of carbon in which every atom is available for chemical reaction from two sides (due to the 2D structure). Atoms at the edges of a graphene sheet have special chemical reactivity.

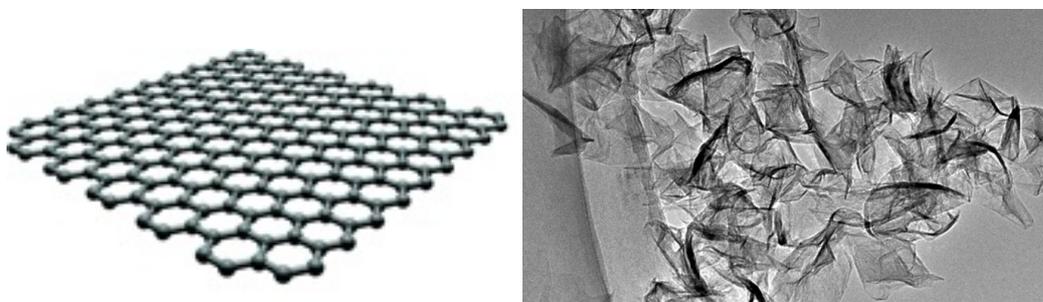


Figure 9.1: Graphene molecular structure and TEM image ⁴⁰

Graphene is the first example of a truly two-dimensional crystal. Its unique structure confers a range of unique and valuable properties, summarised in Figure 9.2 below.

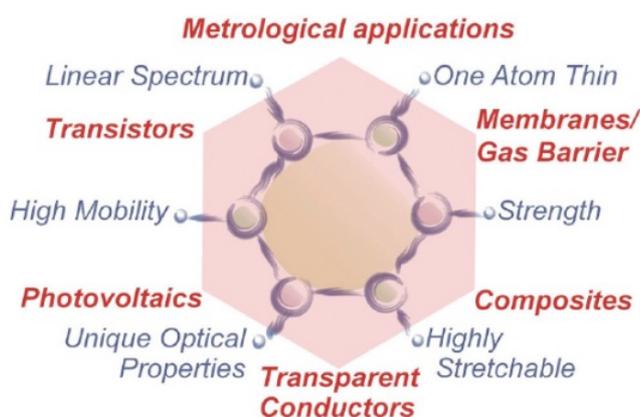


Figure 9.2: Graphene properties and application areas (Ferrari et al. 2015)

⁴⁰ <https://www.nature.com/articles/d41586-018-06103-y>

- ***One atom thin***

Graphene is chemically inert and stable, behaves as an impermeable membrane, and conducts heat and electricity better than any metal. It can absorb gas molecules from the surrounding atmosphere, resulting in doping of the graphene layer with electrons or holes depending on the nature of the absorbed gas. By monitoring changes in resistivity, graphene-based detectors can monitor minute concentrations of certain gases present in the environment (Katsnelson 2007).

- ***Strength***

In proportion to its thickness, graphene is about 100 times stronger than the strongest steel. This makes graphene a desirable addition to lightweight polymers, reinforcing their mechanical properties.

- ***Highly stretchable***

As an ultrathin stretchable membrane, graphene is an ideal material for nonlinear tuneable electromechanical systems.

- ***Unique optical properties***

Graphene is nearly transparent and yet has the ability to sustain extremely high densities of electric current (a million times higher than copper), offering the potential for use in transparent electronic devices (Novoselov et al. 2012).

- ***High carrier mobility***

Graphene displays remarkable electron mobility at room temperature, with reported values in excess of $15000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is an order of magnitude higher than that of modern silicon transistors. The corresponding resistivity of graphene sheets is $10^{-6} \Omega \cdot \text{cm}$, less than the resistivity of silver. Electrons in graphene can cover micrometre distances without scattering, even at room temperature. These unusual electronic properties make graphene a promising candidate for future electronic applications (Katsnelson 2007).

- ***Linear spectrum***

Electrons in graphene obey a linear dispersion relation, behaving like massless relativistic particles. This results in some very peculiar electronic properties – from an anomalous quantum Hall effect to the absence of localization – providing a bridge between condensed matter physics and quantum electrodynamics. Being a gapless semiconductor with a linear energy spectrum, graphene offers potential for developing new electronic devices such as carbon transistors (Katsnelson 2007).

The unique properties of graphene are largely derived from its 2D structure. Only graphene and, to a good approximation, its bilayer have simple electronic spectra and are both zero-gap semiconductors. Anything thicker structures should be considered as thin films of graphite (Geim & Novoselov 2010).

In a sense, ideal defect-less flat graphene is an analogue to diamond, which is a unique material merely because of its mechanical properties, but is of less practical interest for chemical applications. Owing to the delocalised π electrons, graphene is chemically inert and only physisorption on the basal plane is practically possible. However, the edge atoms are extremely reactive and thermodynamically unstable. In many cases, defects and impurities are actually responsible for the electrochemical properties ascribed to graphene materials (Eftekhari & Garcia 2017).

Due to its unique spectrum of valuable properties, graphene is expected to have a major impact in several technological fields. Transparency–conductivity–elasticity can find use in flexible electronics, high mobility and ultimate thinness for use in efficient transistors, while transparency–impermeability–conductivity can be exploited for transparent protective coatings (Ferrari et al. 2015). This creates the potential for a wide range of potential electronic applications, as illustrated in Figure 9.3 below.

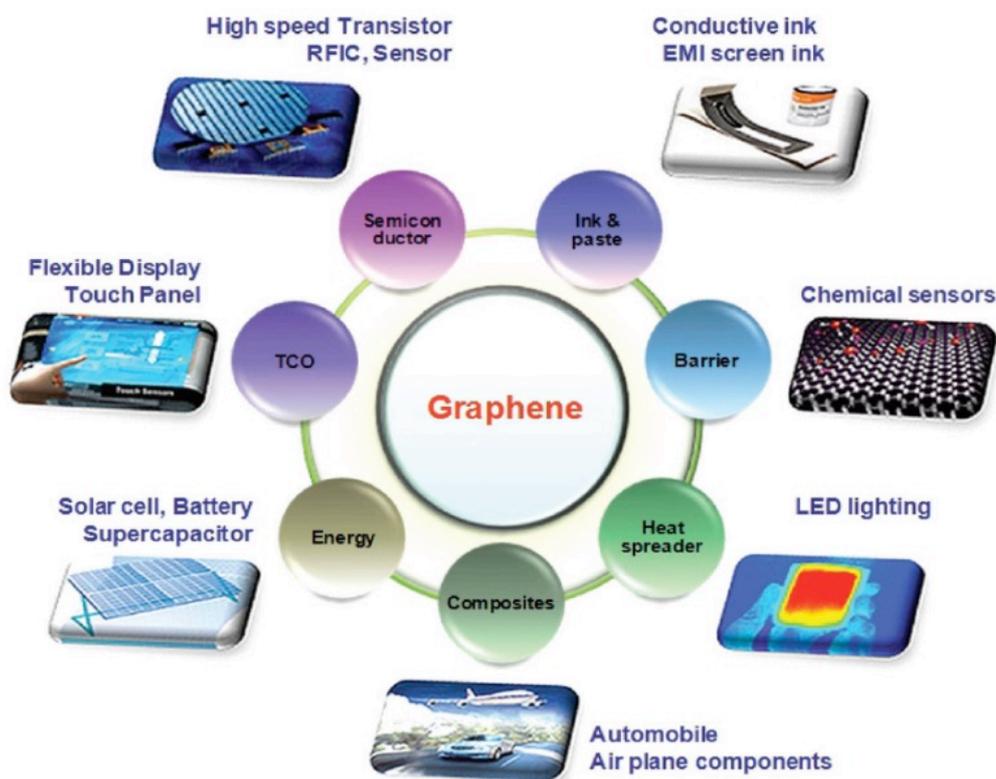


Figure 9.3: Overview of potential applications of graphene

Graphene-based paints can be used for conductive ink, antistatic, electromagnetic-interference shielding, and gas barrier applications (Novoselov et al. 2012).

A large potential market exists in bringing extra functionality to composites, where graphene can contribute gas and moisture barrier properties, electromagnetic shielding, electrical and thermal conductivity, and a strain monitoring capability to the surrounding polymer matrix. As an additive to a

composite matrix polymer it might increase the operating temperature level of composites, reduce moisture uptake, induce antistatic behaviour, give lightning strike protection and improve composite compressive strength (Novoselov et al. 2012).

Chemically functionalized graphene can be readily mixed with other polymers in solution, producing a new class of electrically conductive nanocomposites at relatively low cost (Li & Kaner 2008).

In electronics, potential applications include high-frequency devices, touch screens, flexible and wearable devices, as well as ultrasensitive sensors, nano-electromechanical systems, superdense data storage, photonic devices, etc. (Ferrari et al. 2015).

In the energy field, applications include batteries and supercapacitors to store and transport electrical power, and solar cells. The use of graphene in next-generation lithium-ion batteries is currently being widely studied. It is expected that graphene materials will allow increased power density and higher lithium charge storage capacity. Graphene is also being used to construct supercapacitors for energy storage, where it offers high intrinsic electrical conductivity, an accessible and defined pore structure, good resistance to oxidative processes and high temperature stability (Novoselov et al. 2012).

In the medium term, some of graphene's most appealing potential lies in its ability to transmit light as well as electricity, offering improved performance for light emitting diodes, flexible touch screens, photodetectors, and ultrafast lasers (Ferrari et al. 2015).

In order to capitalise on these opportunities, there is currently intense research under way to develop new graphene-based functional materials with unique properties. These efforts are summarised in Figure 9.4 below.

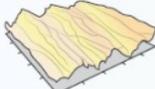
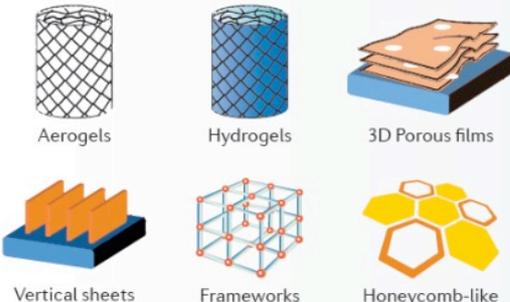
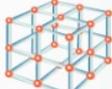
Dimension			Preparation methods	Applications
0D dots			<ul style="list-style-type: none"> • Templated reduction of GO (REF. 89) • Cage opening of fullerene C₆₀ (REF. 6) • Spray-assisted deep frying (REFS 5,93) 	<ul style="list-style-type: none"> • Energy storage • Fluorescent QDs • Electrochemical biosensors • Drug delivery • Bioimaging • Photovoltaics • Composites • Water splitting
 Nanospheres	 Hollowspheres	 Quantum dots		
1D linear structures			<ul style="list-style-type: none"> • Molecular assembly⁸⁴ • Unzipping of CNT⁹⁵ • Wet spinning⁹⁶ • CVD using Cu nanowire template¹³ • Hydrothermal using Cu wire template⁹⁷ • CVD using AAO template¹⁴ 	<ul style="list-style-type: none"> • Microscale energy storage devices • Wearable electronics • Bioimaging • Transparent conducting electrodes • Thermal energy storage
 Ribbons	 Tubes	 Springs		
2D films			<ul style="list-style-type: none"> • Micromechanical cleavage⁴ • Photoexfoliation⁴ • Liquid-phase exfoliation⁴ • Growth on SiC⁴ • CVD⁴ • Molecular beam epitaxy⁴ • Chemical synthesis⁴ • Chemical exfoliation^{19,98} • Chemical under gaseous flow⁹⁹ • Chemical activation¹⁰⁰ • Block copolymer lithography¹⁰¹ • Wet spinning¹⁰² • CVD with metal mesh¹⁰³ • Induced edge nucleation¹⁰⁴ 	<ul style="list-style-type: none"> • Photonic and optoelectronic devices • Energy storage and conversion • Photovoltaics • Sensors • Lubricants • Catalysts • Thermal management • Drug delivery
 Sheets	 Curved sheets	 Porous sheets		
 Nanomesh	 Non-woven mat	 Woven fabrics		
				
3D monoliths			<ul style="list-style-type: none"> • Templated synthesis^{105,106} • Self-assembly¹⁰⁷ • Laser scribing^{55,56} • Thermal¹⁰⁹ • Microwave and chemical activation¹⁰⁰ • Vacuum filtration⁶⁰ • Freeze-drying¹¹⁰ • Crosslinking¹¹¹ • Chemical assembly¹¹²⁻¹¹⁴ • 3D printing¹⁵ 	<ul style="list-style-type: none"> • Absorber for environmental remediation • Energy storage • Sensors • Biosensors • Catalysis • Electrochemistry • Fuel cells • Gas absorption • Hydrogen storage • Water splitting • Scaffold for electronic and biomedical applications • Tissue engineering and regeneration
 Aerogels	 Hydrogels	 3D Porous films		
 Vertical sheets	 Frameworks	 Honeycomb-like		
				
4D self-folding structures			<ul style="list-style-type: none"> • 4D printing? • Other methods? 	<ul style="list-style-type: none"> • Self-healing batteries • Self-folding materials • Materials with on-demand shape transformations from one state to another

Figure 9.4: Synthesis and assembly of graphene structures. AAO, anodic aluminium oxide; CNT, carbon nanotube; CVD, chemical vapour deposition; GO, graphene oxide; QDs, quantum dots. (El-Kady et al. 2016)

9.1.2 Production of graphene

The large-scale industrial use of graphene will require large scale and cost-effective production methods, while providing a balance between ease of fabrication and final material quality, with the properties tailored to suit the final application. The definition of “quality” of a graphene material cannot be given in absolute terms, but strictly depends on the applications. For example, the “quality” of graphene needed for high performance electronics is “the opposite” of that required for batteries or supercapacitors, in that the latter work better with materials having defects, voids and cavities, while the former require defect free, and flat material. This will be a challenge for standardisation, since the materials properties will have to be defined in relation to a variety of possible applications (Ferrari et al. 2015).

The intense interest in graphene has led to the development of a wide range of alternative manufacturing processes, which are illustrated in Figure 9.5 below.

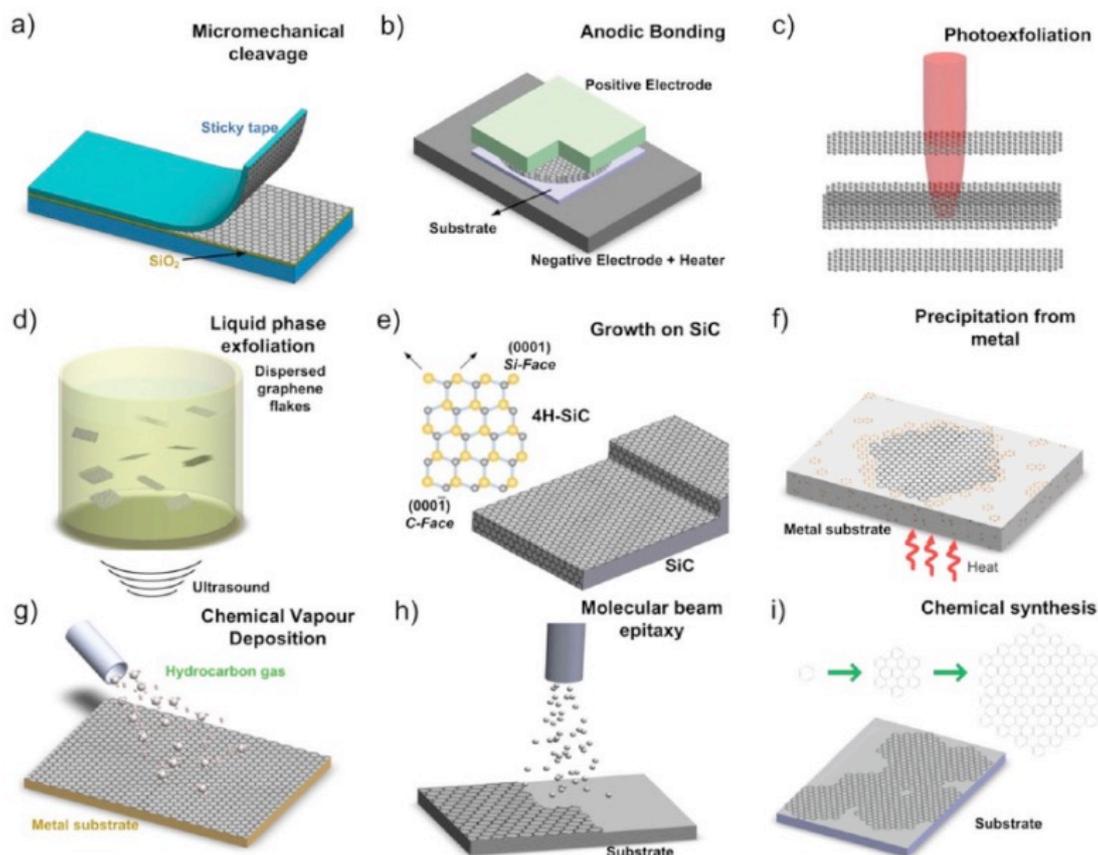


Figure 9.5: Schematic illustration of the main experimental setups for graphene production. (a) Micromechanical cleavage (b) Anodic bonding (c) Photoexfoliation. (d) Liquid phase exfoliation. (e) Growth from SiC. Schematic structure of 4H-SiC and the growth of graphene on SiC substrate. Gold and grey spheres represent Si and C atoms, respectively. At elevated temperatures, Si atoms evaporate (arrows), leaving a C-rich surface that forms graphene. (f) Precipitation from carbon containing metal substrate. (g) Chemical vapour deposition process. (h) Molecular beam epitaxy. Different carbon sources and substrates (i.e. SiC, Si, etc.) can be exploited. (i) Chemical synthesis using benzene as building blocks. (Ferrari et al. 2015)

Given that graphite is relatively inexpensive and available in large quantities, the method that has received the most attention for large-scale production of graphene is the top-down method, i.e., splitting graphite into individual sheets either mechanically or chemically. The first isolation of single layer graphene was achieved in 2004, using a “peeling” method in which common cellophane tape was used to successively remove layers from a graphite flake.

In 2006, a solution-based process was developed for producing single-layer graphene. The method involved chemical modification of graphite using potassium permanganate and sulphuric acid (Hummer’s method) to produce a water dispersible intermediary, graphite oxide, which is a layered stack of puckered sheets that completely exfoliates to graphene oxide upon the addition of mechanical energy. Subsequent deoxygenation, by thermal annealing or through treatment with chemical reducing agents, can restore electrically insulating graphene oxide to conductive graphene. Even though the resulting material may contain graphene components with several layers, it still preserves many of the appealing properties of single-layer graphene (Allen et al. 2009). The sequence of reactions involved in top-down production of graphenes using Hummer’s method is illustrated in Figure 9.6 below.

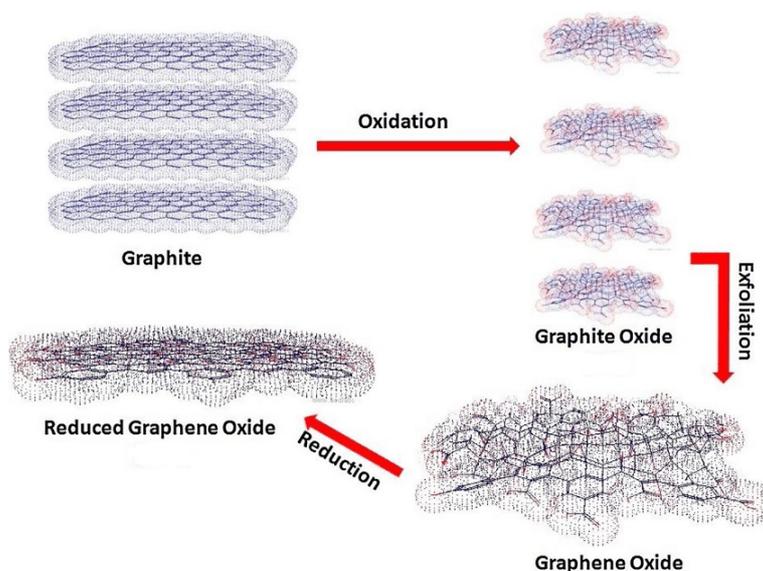


Figure 9.6: Production of graphenes by (i) oxidation of graphite flakes to produce graphite oxide, (ii) exfoliation via sonication to produce graphene oxide, and (iii) chemical or thermal reduction to produce reduced graphene oxide. (Samal & Das 2018).

Chemical or thermal reduction of graphene oxide to reduced graphene oxide (graphene) leaves residual oxygen-containing groups and makes the resulting surfaces negatively charged when dispersed in water. By controlling the colloid chemistry, graphene sheets can form stable aqueous colloids via electrostatic repulsion, enabling the use of low-cost solution processing techniques to fabricate various potentially useful graphene-based materials. For example, graphene films can be made by drop-casting, spraying, electrostatic adsorption, filtration, and dip- or spin-coating of graphene or precursor dispersions (Li & Kaner 2008).

9.2 GRAPHENE OXIDE

There is currently a strong research focus on exploring alternative ways to produce graphene oxide (GO), as an intermediate product that can be subsequently reduced to graphene. GO has the same structure as graphene, with the addition of oxygen-containing functional groups (carboxyl and hydroxyl) on the basal planes and edges that provide reactive sites for chemical modification. GO can be easily dispersed in water, is easy to process, and can readily be produced in large quantities (Khan et al. 2017).

GO films can be deposited on any substrate and can be converted into a conductor (via reduction). This makes it suitable for the use in the production of transparent conductive films, flexible electronics, solar cells and chemical sensors. GO has a high surface area and can be suitable for the use as electrode material for batteries and capacitors. GO can easily be mixed with different polymers and other materials to enhance their properties like tensile strength, elasticity and conductivity of composite materials (Khan et al. 2017). The techniques involved in printing GO in both 2 and 3 dimensions, and their applications, have recently been reviewed (Tran et al. 2018).

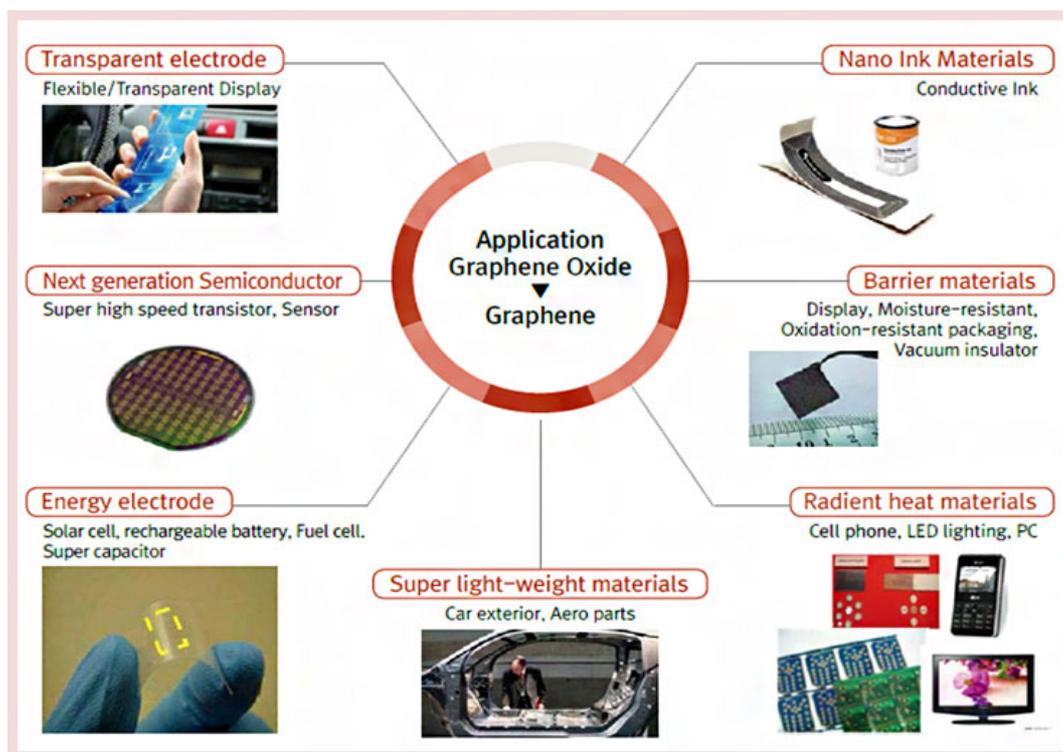


Figure 9.7: Potential applications for graphene oxide⁴¹

⁴¹ <http://www.daejoo.co.kr/sub2/sub09.asp?ch=9>

In solid form, GO flakes are attached to one another to form thin and stable flat structures that can be folded, wrinkled and stretched. Such structures can be used for applications in hydrogen storage, ion conductors and nanofiltration membranes (Khan et al. 2017).

9.3 QUANTUM DOTS

9.3.1 Overview of quantum dots

Quantum dots (QDs) (i.e. CQDs and GQDs) represent a new class of materials in which quantum confinement effects are exhibited. They are very small semiconductor crystals, comprising turbostratic (i.e. misarranged sheets) or graphitic carbon (sp^2 carbon) or graphene and graphene-oxide sheets blended with diamond-like sp^3 hybridized carbon additions. The surface of QDs is coated with oxygen-rich moieties which impart high solubility in aqueous solutions and provide the potential for additional functionalization. (Das et al. 2019).

The term 'quantum dot' includes two distinct categories:

- Carbon nano dots with $\leq 10\text{nm}$ size with a crystal lattice structure, known as carbon quantum dots; and
- Graphene nanosheets with a plane size $< 100\text{nm}$, known as graphene quantum dots (Zhu et al. 2015; Das et al. 2019).

QDs are distinguished from a third category of carbon nanomaterial:

- Carbon nano dots with $\leq 10\text{nm}$ size without a crystal lattice structure; known as amorphous carbon dots.

Collectively, these three types of carbon materials are known as carbon nano dots (Zhu et al. 2015).

QDs were first discovered in 2004 and since then have been subject to intensive research activity, due to their broad range of potential application in the fields of energy conversion and storage (photovoltaic devices, light-emitting diodes, photodetectors, thermoelectric devices, supercapacitors and rechargeable batteries), synthesis (photocatalysis and electrocatalysis), and biomedical applications (cellular and in vivo imaging, biosensors, photothermal and photodynamic therapy) (Yan et al. 2019), as summarised in Figure 9.8 below.

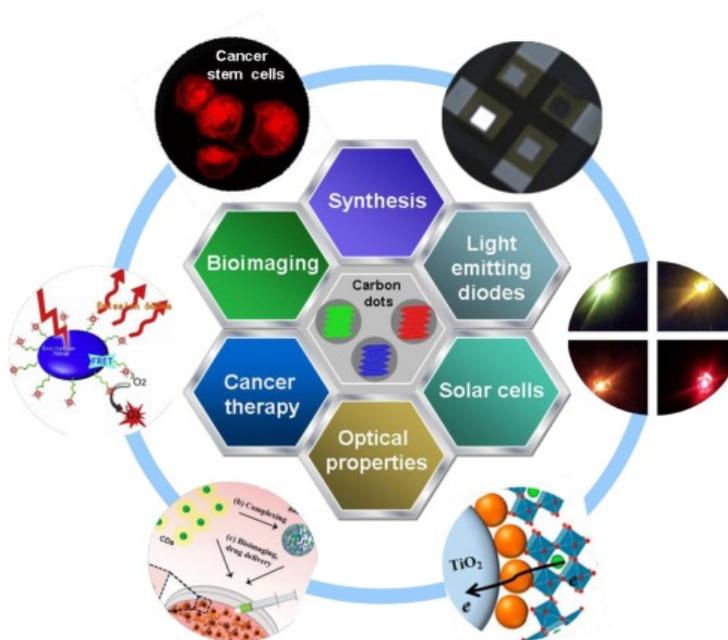


Figure 9.8: Applications of quantum dots (Yuan et al. 2016)

QDs have been found to exhibit the unique characteristics of low toxicity, chemical inertness, biocompatibility and cost effectiveness (Das et al. 2019).

The crystalline core of QDs contains up to about a thousand atoms, which tightly confine electrons or electron-hole pairs called “excitons” in all three dimensions – known as the quantum confinement effect (Kumar et al. 2018). The combination of size, functional surface groups and quantum confinement effect confers distinctive properties to QDs such as infrared-responsive up-converted photoluminescence (UCPL), tuneable photoluminescence (PL), and distinctive photo-induced electron transfer (Das et al. 2019).

These properties can be specifically tuned to have a desired output by altering the dot size and shape. For example, when QDs are excited by a photon of energy, those of comparatively larger size, at around 5–6 nm, emit energy in the wavelength of orange or red, while smaller QDs emit shorter wavelengths in the blue or green range (Kumar et al. 2018).

As-prepared QDs always possess many reactive groups, which are susceptible to reaction with organic molecules, which may cause the disappearance of the optoelectronic properties. Surface passivation, involving the addition of a thin, insulating capping layer, is essential to shield QDs from the adhesion of impurities and improve their fluorescence intensity (Dimos 2016).

9.3.2 Synthesis of quantum dots

The synthesis of QDs can be achieved using either top-down nano-cutting methods or bottom-up organic approaches.

Top-down nano-cutting generally involves oxide cutting of different carbon resources such as graphite powder, GO, carbon fibres, carbon nanotubes, carbon black, and even candle soot. A two-step cutting process is usually used. The first step involves converting graphite-based material into GO sheets, typically usually using the modified Hummers method with a concentrated oxidizing acid (HNO₃ or a mixture of H₂SO₄/HNO₃). The second step involves cutting the GO into QDs using various methods (Zhu et al. 2015).

The “bottom-up” methods are efficient routes to produce fluorescent CDs on a large scale. This approach utilises organic compounds containing –OH, –COOH, –C=O, and –NH₂ groups that can dehydrate at elevated temperatures. There are many approaches for carrying out the dehydration and carbonisation processes, such as hydrothermal, microwave, and combustion methods, pyrolysis in concentrated acid, carbonisation in a microreactor, enhanced hydrothermal (microwave-hydrothermal and plasma-hydrothermal) methods. It is difficult to control these formation processes, resulting in polydisperse QDs (Zhu et al. 2015).

The functional properties of the QDs are dependent on both the source material and the synthesis route, plus any subsequent surface functionalisation and passivation steps. This makes it possible to tailor the performance of the QDs to suit the requirements of specific applications.

As is the case for pure graphene oxide, it is possible to produce graphene by reduction of quantum dots. QDs contain a graphitic/graphenic core and can thus be considered smaller homologues of graphene. Under thermal or chemical reducing conditions, QDs can anneal to form extended sheets of graphene domains.

9.4 QUANTUM DOTS AND GRAPHENE FROM HUMIC ACID

In researching this report it became apparent that there are correspondences between quantum dots and humic acid that have not hitherto been recognised.

The association between QDs and humic acid began with investigations at Rice University in Houston, Texas, where efforts were made to find a cheaper way to produce QDs than extraction from graphite. It was found that QDs can be extracted from bituminous coal and anthracite using concentrated sulphuric acid and nitric acid. The synthesized QDs, produced in up to 20% yield from coal, had a diameter of 2.96 ± 0.96 nm and exhibited blue fluorescence in aqueous solution (Ye et al. 2013).

The Rice University process has been patented (Tour et al. 2018) and licensed to Dotz Nano Ltd, based in Israel, which specialises in the development and marketing of QDs used for tracing, anti-counterfeiting and product-liability solutions.⁴²

The Rice University researchers seem to be unaware of the fact that the process of extracting coal with concentrated nitric acid has long been used by coal scientists to liberate humic acid. For

⁴² <https://www.dotz.tech/>

example, Charmbury et al. (1945) stated: “The partial oxidation of coals yields acidic substances which resemble the naturally occurring humic acids of peat and brown coals in many respects. A particularly effective oxidising reagent for this purpose is concentrated nitric acid because of the rapidity with which it attacks coal and yet does not carry the oxidation appreciably beyond the humic acid stage.”

The pioneering research at Rice University stimulated other investigators to look at low grade coals as sources of QDs, and even humic acids have been shown to contain humic acid. Consequently, a series of correspondences have emerged between QDs and humic acid which collectively suggest that humic acid is either a rich source of QDs, or indeed that humic acid is a type of QD. These correspondences, which are summarised in Table 9.1 below, extend beyond mere physical similarity to include similar growth-promoting effects on plants.

	Quantum dots	Humic acid
	Quantum dots can be produced by oxidation of coal with concentrated nitric acid (Ye et al. 2013).	Oxidation with nitric acid is a well-established method to produce humic acid from coals (Charmbury et al. 1945).
Extraction from coal	QDs can be extracted from sub-bituminous coal with hydrogen peroxide (Das et al. 2019).	Hydrogen peroxide is used to increase the humic acid content of low rank coals (Anillo-Correa et al. 2013).
		Natural QDs were found to be present in humic acid and fulvic acid extracted from low rank coal using alkali (Dong et al. 2015).
Nanometre size	Quantum dots have a maximum diameter of $\leq 10\text{nm}$ (Zhu et al. 2015).	Humic acid forms spherical particles with maximum diameter of about 3.5nm (Pranzas et al. 2003)
Graphitic structure	Quantum dots are very small semiconductor crystals with a carbon content of 60% to 90% (Wang et al. 2019), comprising turbostratic or graphitic carbon (sp^2 carbon) or graphene and graphene-oxide sheets blended with diamond-like sp^3 hybridized carbon additions (Das et al. 2019).	Humic acid from low rank coal contains graphitic material with turbostratic structure, comprising stacked fractions of several layers composed of aromatic structures and minor aliphatic structures (Xavier et al. 2012). About 75% of the carbon in humic acid from leonardite is aromatic (Ricca et al. 1993).
Photoluminescence	Quantum dots exhibit photoluminescence through a combination of size, functional surface groups and quantum	Both humic acid and fulvic acid exhibit weak visible fluorescence when excited by light at 465nm. Electron-

	confinement effect (Das et al. 2019).	donating functional groups attached to aromatic nuclei are responsible, at least in part, for the fluorescence (Ghosh & Schnitzer 1980).
	Hydrothermal treatment (180°C for 6h) was developed as a 'green' method to reduce graphene oxide to stable graphene solution (Zhou et al. 2009).	Hydrothermal catalytic reduction used to convert humic acid to a reduced graphene oxide material dubbed 'graphenol' (Beall 2014).
Reduction to graphene	Quantum dots were reduced to graphene by thermal annealing and infrared laser irradiation (Strauss et al. 2018).	Potassium humate was reduced to graphene by thermal annealing at 700°C (Huang et al. 2016). Humic acid was reduced to graphene on copper foil substrates by thermal annealing in an atmosphere of Ar and H ₂ at temperatures between 1050°C and 1100°C (Beall et al. 2014).
Plant growth stimulation	Quantum dots have been shown to stimulate the growth of wheat (Tripathi & Sarkar 2015), lettuce (Zheng et al. 2017) and mung bean (Wang et al. 2018). Graphene oxide can be blended with plant macronutrients to produce slow release fertilisers with improved physical properties (Kabiri et al. 2017a; 2017b, Andelkovic et al. 2018; 2019).	Humic acid is well known for its ability to stimulate the growth of plants (Rose et al. 2014). Slow-release nitrogen fertilisers can be produced by granulating humic acid with urea (Liu et al. 2009, Jinhua et al. 2012) or humic-rich Victorian lignite with urea (Saha et al. 2017; 2018; 2019).

Table 9.1: Correspondences between quantum dots and humic acid

Despite all these correspondences, a fundamental difference between quantum dots and humic acid lies in the structure of the carbon molecules in the core of each nanoparticle. Ideal quantum dots contain a crystalline core comprising carbon with a graphitic structure. In contrast, the carbon rings at the core of humic acid nanoparticles have a turbostratic structure, which lacks the electrically conductive properties of graphite.

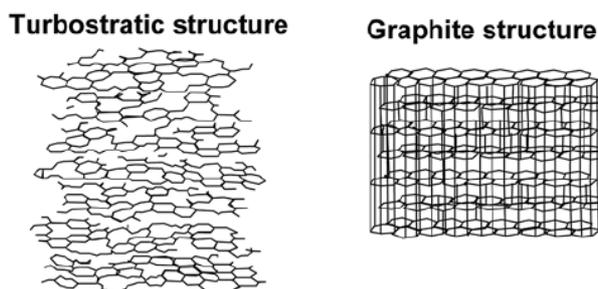


Figure 9.9: Turbostratic versus graphitic structure of carbon

However, at the nanometre scale, the turbostratic structure can be converted to graphitic under relatively mild conditions. One of the unique properties of graphene is that it is self-repairing. The free energy of defect sites is sufficiently high that any free aliphatic carbon groups will be utilised to fill the gaps in damaged graphene sheets (Vicarelli et al. 2015). Also, it is well known that one of the characteristic features of nanosystems is their high surface-to-volume ratio. As a result, nanoparticles such as quantum dots and humic acid have a very high Gibbs free surface energy, which provides a driving force for molecular rearrangement via Ostwald ripening (Wang & Yang 2005).

As an example, researchers at the Henan Polytechnic Institute in China recently demonstrated that humic acid can be converted to graphene oxide by hydrothermal reaction in water at 190°C for 10h. The resultant homogeneous mixture was sonicated and centrifuged to obtain a brown solution of graphene oxide (GO), as shown in Figure 9.10 below. Reduced GO (r-GO, i.e. graphene) was further prepared from GO by thermal reduction at 900°C for 40 s under N₂ atmosphere (Huang et al. 2018).

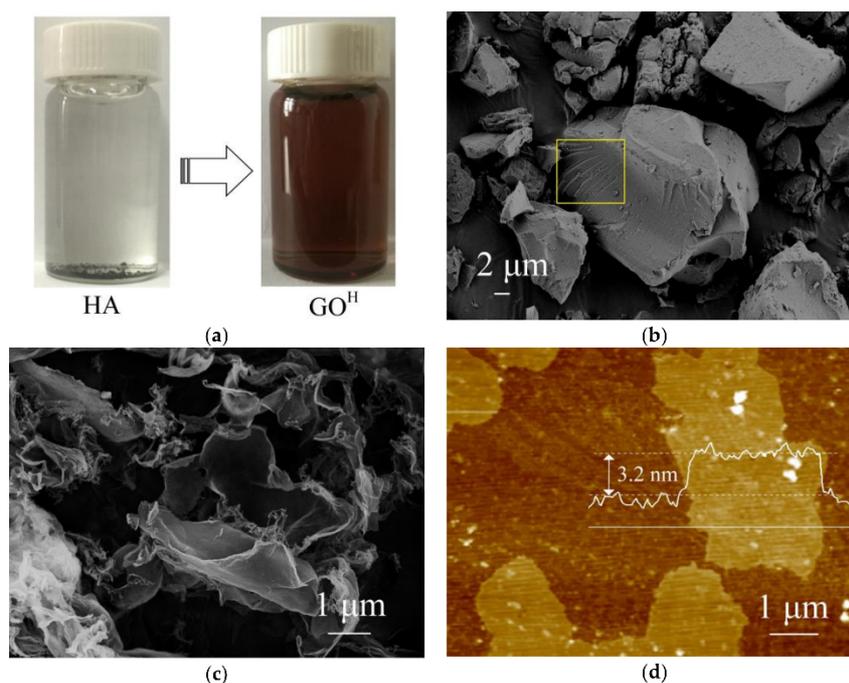


Figure 9.10: (a) A photograph of humic acid (HA) and as-prepared Graphene Oxide (GO) solution; (b) Scanning electron microscopy (SEM) image of HA; (c) SEM of GO; (d) Atomic Force Microscopy (AFM) of r-GO (Huang et al. 2018)

These researchers concluded that non-aromatic components within the humic acid can self-assemble into graphitic hexagonal matrix under hydrothermal conditions, resulting in an increased sp^2 carbon content of GO. Thermal reduction of the GO produced thin and transparent films, with similar morphology, crystalline structure and composition to r-GO prepared by liquid-phase exfoliation of graphite. The r-GO delivered considerable area capacitance, high rate capability and good electrical conductivity (Huang et al. 2018).

There are thus compelling reasons to suggest that humic acid may represent a low cost intermediate for production of new products based on graphene, graphene oxide and quantum dots. The fact that humic acid can be readily extracted from Victorian lignite using a relatively mild alkali process suggests that humic acid has potential as a low cost- bulk intermediate for large scale fabrication of graphene-based devices. A directed program of research is needed to investigate this possibility.

9.5 VICTORIAN RESEARCH CONTEXT

Swinburne University and Sydney-based company, Cleantech Energy Australia Pty Ltd, have formed a joint venture company called GrapheneX as a vehicle for research on graphene and graphene quantum dots.

The focus of GrapheneX is the development of processes for low-cost production of graphene oxide and the fabrication of advanced materials and processes based on graphene. The research draws upon the skills of Dr Nishar Hameed, who has expertise in graphene nanocomposites and functional materials, and Professor Baohua Jia, who has expertise in fabrication of graphene oxide supercapacitors, graphene metamaterials, 3D graphene networks and advanced solar cells.

The goal of GrapheneX is to develop next-generation low-emission energy technologies that capitalise on the unique properties of graphene and graphene oxide.

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10 Conclusion

This report has highlighted the range of carbon materials that could be produced from the large quantities of inexpensive lignin and lignite that are available in the Latrobe Valley, and their potential applications, as summarised in Table 10.1 below.

Carbon Product	Potential Applications
Briquettes	Industrial fuel for steam, hot water and kilns, gasification feedstock, feedstock for metallurgical char and activated carbon production.
Lignin from papermaking	Foam fire extinguishers, printing inks, extender/modifier, rubber compounding, phenolic resins, surfactants, epoxy resins, adhesives and bioplastics.
Metallurgical char	Ferroalloy production, ironmaking, recarburising of steel, anodes for aluminium smelting, reductant for mineral sands.
Activated carbons	Treatment of drinking water, groundwater, municipal wastewater, industrial wastewater; remediation of contaminated groundwater and soil; air and gas cleaning; solvent recovery; gas storage; and in industrial production processes such as in pharmaceuticals, chemicals, food and beverage production.
Humic substances	Stimulation of plant growth, solubilisation of essential plant trace elements, improved chemical fertilisers, animal feed supplements.
Carbon fibres	
High tensile carbon fibres	Aircraft, automobiles, boats, machine parts, high-grade sporting goods, pressure vessels, wind turbine blades, civil engineering.
Chopped carbon fibres	Disk brake pads, gaskets for gas sealing, seal rings and packings, insulating components.
Electrospun carbon fibres	Textiles, air filters, catalyst supports, medical applications, electrodes for lithium-ion batteries, supercapacitors, in solar cells and sensors, adsorbents.
Activated carbon fibres	Water purification, heavy metal removal, odour control, SO ₂ and NO _x removal, biomedical applications, capacitors, vapour sensing, refrigeration, catalysis, electrochemical applications, natural gas and biogas storage, wound dressings, medical personnel masks and blood purification.
Graphene-based products	
Graphene	Conductive ink, flexible touch screens, chemical sensors, solar cells, batteries, supercapacitors, LED lighting, automobile and aircraft components, electromagnetic-interference shielding, gas barrier, flexible and wearable devices, nano-electromechanical systems, superdense data storage, improved performance for light emitting diodes, ultrafast lasers.
Graphene oxide	Water-dispersible precursor for graphene; hydrogen storage, ion conductors, nanofiltration membranes.
Quantum dots	Photovoltaic devices, light-emitting diodes, photodetectors, thermoelectric devices, supercapacitors, rechargeable batteries, catalysis, cellular and <i>in vivo</i> imaging, biosensors.

Table 10.1: Range of potential applications for carbon products that could be produced in Victoria

The applications have the potential to impact on every aspect of modern life, covering heavy industry, agriculture, renewable energy production and storage, automotive and aerospace, clean food and water, biomedicine and consumer electronics.

Currently, there is only one commercial business in the Latrobe Valley that is manufacturing carbon products from local resources. Omnia Specialities Australia in Morwell extracts humic substances (humic acid and fulvic acid) from lignite, for use in agriculture both in Australia and overseas. Lignite itself is well known to be a beneficial soil amendment, increasing organic carbon in depleted soils and thereby increasing plant yields and drawdown of atmospheric CO₂. Humic substances extracted from weathered lignite have found a wide range of potential applications in agriculture, including stimulation of plant growth, solubilisation of essential plant trace elements, blended with chemical fertilisers and as animal feed supplements.

If similar levels of humic substances can be extracted from 'as mined' lignite, this would drop the production cost significantly and lead to the expansion of a major new industry sector. ACI is helping to support the growth potential of Omnia Specialities by funding a research project at the Carbon Technology Research Centre at Federation University, Churchill, to investigate improvements in the production of humic substances from run-of-mine lignite. The aim of this project is to facilitate efficient humic extraction from a greater proportion of the lignite resource, thereby removing a bottleneck to greater export sales.

Up until 2014, there were two other viable businesses in the Latrobe Valley producing value-added carbon products from Victorian lignite. The Energy Brix briquette factory in Morwell produced briquettes as a supplementary start-up fuel for the Loy Yang, Yallourn and Hazelwood power stations, for steam generation in regional factories lacking access to natural gas, and as a feedstock for char production. Australian Char in Morwell converted briquettes into export-grade char products for use in ferroalloy production and steel recarburisation, as well as the iconic 'Heat Bead' barbeque fuel.

These two businesses were forced to close in 2014 as a result of the shut-down of the Energy Brix power station, which was one of the oldest and least efficient in Victoria. However, an opportunity exists to reopen these businesses, which is being explored by several commercial interests. A start up business has commenced briquette manufacturing, however this at small scale. Briquetting is both an important part of Victoria's industrial past and an underpinning technology for carbon upgrading technologies, and as such there is a relevant role for it into the future.

Australian Paper in Maryvale produces large quantities of lignin-rich 'black liquor' as a byproduct of its papermaking operations, which is currently burned to produce process steam. A portion of this stream could be upgraded to produce purified Kraft lignin as a feedstock for value-added carbon products. This possibility is currently being investigated at Federation University in Churchill and by the ARC Hub for Processing Advance Lignocellulosics into Advanced Materials, at Monash University.

Research and development is currently under way to create value-added carbon products from Victorian lignite. Environmental Clean Technologies has developed technologies for producing iron by direct reduction of iron ore with lignite, which it is seeking to commercialise in India. A research team at Monash University, led by Professor Alan Chaffee, has developed novel intellectual property

around production of honeycomb activated carbon monoliths and blast furnace coke from lignite, and is seeking support for commercialisation. Development of both of these technologies was initially supported by Brown Coal Innovation Australia, forerunner to ACI.

ACI is also funding Professor Chaffee in a collaborative project with Associate Professor Minoo Naebe, at Carbon Nexus, Deakin University in Geelong, to investigate the possibility of producing low cost carbon fibres from Victorian lignite. This is an initial, proof-of-concept exploration of the potential to fabricate carbon fibres suitable for use in the high volume automotive industry. This project is positioned to take advantage of the potential synergies between the low cost lignite resource in the Latrobe Valley and carbon fibre manufacturing capabilities at Carbon Nexus. The project will identify suitable market opportunities for carbon fibres produced from Victorian lignite, and develop strategies for industry engagement to facilitate further research and development.

It is likely that extraction of carbon fibre precursor from lignite will create residual char. Extensive prior research has shown that high grade activated carbon products can be manufactured from char. Early research also investigated the possibility of fabricating anodes for aluminium smelting from lignite char. The results were encouraging, but the research was shelved in the mid-1980s due to the ready availability and low cost of the main anode ingredient, calcined petroleum coke. However, there is currently a worldwide shortage of calcined petroleum coke, pushing up prices and creating difficulties for the aluminium smelting industry. It appears that there may be a market opportunity for acid-leached Victorian lignite char as a partial replacement for calcined petroleum coke in carbon anodes. It is recommended that a cost analysis study be undertaken in consultation with Australian aluminium smelters, to determine whether there would be sufficient cost incentive to allow commercial consideration of a lignite char alternative. If this looks promising, then a trial evaluation program could be undertaken in collaboration with local smelters who fabricate anodes in-house.

Graphene is currently the advanced carbon material that is generating the greatest development buzz. In order to fulfil its commercial potential, great efforts have been made to find a way to mass-produce graphene at low cost. Most attention has been given to extracting graphene from graphite, via the water-dispersible intermediate product, graphene oxide, and a nano-scale derivative, quantum dots. However, the standard method has the drawbacks involving toxic and potentially explosive chemicals. Recent research has shown that graphene oxide and quantum dots can be extracted from bituminous coal and lignite, offering a lower-cost manufacturing route.

There is a compelling case to suggest that humic acid, extracted from lignite, is a rich source of quantum dots, with the potential to be further upgraded to graphene oxide and graphene. Humic acid is already produced by Omnia Specialities as an agricultural input, suggesting the potential for the Latrobe Valley to become a supplier of a low cost intermediate for large scale fabrication of graphene-based devices. Investigation of this opportunity is on the agenda of GrapheneX, a start-up joint venture between Swinburne University and Cleantech Energy Australia, which is developing next-generation low-emission energy technologies that capitalise on the unique properties of graphene and graphene oxide.

The research activities that have been highlighted in this report represent very early-stage efforts to capitalise on the opportunities presented by the Latrobe Valley's rich carbon resources for production of high value, next-generation carbon products. The possibilities have been explored by a small number of research groups with relatively little funding. The reality is that Victoria has an abundance of research groups that have expertise in advanced carbon materials which could be brought to bear on this problem. Table 10.2 below lists the Victorian research groups that are involved in the Australian Nanotechnology Network ref⁴³, with skills and resources in the allied areas of nanomaterials, nanofabrication, photonics, solar cell fabrication, batteries and supercapacitors, optoelectronics, biosensors, membranes, carbon fibres and composite materials.

Research Group	Location
Applied NanoBioTech Group	RMIT
ARC Centre of Excellence for Nanoscale BioPhotonics	RMIT
ARC Centre of Excellence in Convergent Bio-Nano Science & Technology	Monash University
ARC Centre of Excellence in Exciton Science	University of Melbourne
ARC Centre of Excellence in Future Low-Energy Electronics Technologies	Monash University
Carbon Biomaterials Group	University of Melbourne
Centre for Micro-Photonics	Swinburne University of Technology
Centre for Material and Fibre Innovation	Deakin University
Department of Chemical Engineering	Monash University
Department of Materials Engineering	Monash University
Devices, Systems and Engineering Program	CSIRO Division of Materials Science and Engineering
Flexible Electronics Theme	CSIRO
Functional Materials and Surface Groups	Swinburne University of Technology
Institute for Frontier Materials	Deakin University
Materials Modelling and Simulation Group	RMIT
NanoSafe Australia	RMIT
Nanotechnology Victoria Ltd	Monash University
Sensing Technology Lab	Swinburne University of Technology
Sensor Technology Lab	RMIT
Textile and Fibre Technology	CSIRO

Table 10.2: Research groups in Victoria active in next generation carbon materials

⁴³ <http://ausnano.net/index.php?page=groups>

This suggests that Victoria is well placed to take advantage of the wide range of opportunities that exist for producing that next-generation carbon products that will underpin the advanced technologies of the 21st century. The Latrobe Valley is rich in carbon resources and has the skilled resources needed to transform them into export-ready products. Complementing these are the skilled scientists and research infrastructure available in Victoria's universities and at CSIRO. All the ingredients are available for Victoria to become a world leader in the production of high value, next-generation carbon products.

There is a caveat, however. Currently 99.99% of all lignite and 100% of all lignin is used for energy production. Under current policy settings and economic imperatives it is likely that there will be no power production from lignite by the 2040's or perhaps even earlier. This means the Latrobe Region has a short period to transition from using lignite and lignins as fuels to developing their potential as raw material for advanced carbon products and agricultural applications. It is well known that it takes between 10 and 20 years to develop products from concept to commercialisation, so the transition must start now.

As with the development of the power industry in the early twentieth century this transition must be led by the State government with support by the Commonwealth government. The government of the day post-World War 1 recognised the long term need to utilise the value of lignite for low cost power production, and devoted the necessary resources to develop the technology and industry that allowed Victoria to become the manufacturing powerhouse of Australia.

What is urgently needed now is the vision and the willingness to capitalise on the opportunities highlighted in this report, and financial support for commercially-focussed research and development. The initial investment to 'kick start' these new carbon industry sectors must come from government, particularly in the research and smaller scale demonstration phases. Past experience has shown that industry will invest when the government demonstrates its confidence in the sector.

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