



Lignin Valorisation Opportunities From Cellulosic Sugar Production

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1 Executive Summary

At present, the majority of lignin generated around the globe originates from either an acid sulfite or a kraft pulping process. However, with regards to cellulosic ethanol production, neither the kraft process nor the acid sulfite pulping processes are compatible pretreatment techniques, due to substantial costs associated with the generation of high quality cellulose for pulp and paper manufacturing. Alternative pretreatment technologies include: alkali, dilute acid, concentrated acid, liquid hot water, steam explosion, AFEX, and organosolv processes. All of these technologies, with the exception of concentrated acid, AFEX and organosolv, are available for the pretreatment of lignocellulosic biomass at commercial scales.

In terms of lignin recovery, steam explosion, organosolv, and alkaline pretreatments demonstrate the highest attainable yields. Followed by concentrated acid, dilute acid, and liquid hot water pretreatments. These pretreatment technologies generate a wide range of molecular weight lignins. Those that produce higher molecular weight lignins include dilute acid, concentrated acid and AFEX pretreatments, whereas alkaline, liquid hot water, steam explosion and organosolv pretreatments produce lower molecular weight lignins. In general, all lignin fractions display a high number of phenol and hydroxyl groups. The presence of β -O-4 linkages and other labile bonds tends to correspond with the degree of lignin depolymerization, i.e. smaller lignin fragments generally contain less of these reactive sites as they have been more extensively degraded. Higher molecular weight lignins are therefore, typically more reactive than lower molecular weight compounds.

With regards to biomass compatibility, in general all pretreatment technologies are suitable for processing agricultural residues. Therefore, when considering the types of feedstocks that are readily available in Indonesia (e.g. rice/maize straw, oil palm empty fruit bunches, sugarcane residues and bagasse), all technologies could potentially be used as a means of pretreating biomass prior to cellulosic ethanol production. In terms of wood processing, hardwoods are largely compatible with all pretreatment processes apart from AFEX, and softwoods are believed to be processed most effectively using liquid hot water pretreatment.

There are two main options for the technical development of pretreatment derived lignins: 1) to take advantage of established markets for liginosulfonates through the sulfonation of suitable pretreatment lignins; and 2) to establish new applications based on those currently under development for kraft lignins.

In terms of identifying interesting market opportunities for pretreatment derived lignins, there are a number of factors that must be considered and these form the basis of this review. These include:

- 1) The TRLs of the applications in question (i.e. is there an existing market to sell into?);
- 2) The suitability of the lignin for the given application (i.e. do the properties of lignin match up to those required for the application?);
- 3) The value of the application (i.e. is the chosen application/market likely to yield good economic returns?).

Based on these key factors, a near-term market opportunity has been identified in the production of biomass pellets for heat applications. This is an existing application that has been developed

commercially for lignosulfonate/kraft lignin use. The properties of lignins derived from pretreatment appear to be compatible with this function. However, this is a low-value market application and thus, it may be more profitable to target an end-use that could yield better returns.

Another interesting near-term application is in the production of phenol formaldehyde resins. The phenolic properties of lignin make it an ideal candidate to replace fossil-derived phenol. This application has been extensively developed using kraft lignin and at present, is considered technically ready for commercialization.

Although less developed than phenol formaldehyde resins, the production of carbon fiber for use in composites is also considered an attractive target for lignin product development. Although technical restrictions may prohibit their use in high performance applications such as aerospace, there could be an opportunity to incorporate these materials into automotive applications for example, as part of industry efforts to enhance the light weighting of vehicles.

Finally, the conversion of pretreatment derived lignins into water soluble lignosulfonates may also be possible depending on the target application, and on technical requirements such as molecular size or distribution. This offers up a wider range of possible applications to these types of lignins.

In all of the possible end-uses outlined above, it is important to be aware however, that any novel lignins entering the market will not only compete with fossil-based alternative materials, but also with the conventional lignins that currently dominate the lignin market (i.e. kraft lignins and lignosulfonates). Therefore, any commercial project targeting specific lignin applications will require a detailed techno-economic and market analysis to determine the true extent of the opportunity proposed.

2 Introduction

Transport is responsible for generating around one quarter of the world's annual CO₂ emissions¹ - it has played a critical role in exacerbating the harmful effects of global warming and climate change. In efforts to minimize the impacts of fuel combustion, many countries have now introduced policies and legislation to support the uptake of new renewable transport fuels with lower associated greenhouse gas (GHG) emissions. The two fuels that currently dominate this market are fatty acid methyl esters (FAME) and bio-based ethanol.

FAME is traditionally blended with fossil-diesel and derived from the transesterification of vegetable oils. While bio-ethanol is blended with gasoline (petrol) and is obtained *via* the fermentation of sugars derived from agricultural feedstocks. Typical sources of fermentable sugars include starch from cereal crop grains (e.g. maize, wheat, cassava) and sucrose from sugar crops (e.g. sugar cane and sugar beet). The use of either starch or sucrose as process feedstocks offers a relatively inexpensive route to ethanol production. However, the cultivation of appropriate crops (particularly annual crops such as maize, wheat and sugar beet) is often associated with sustainability and environmental concerns, such as land use issues (i.e. competition with food production) and emissions linked to fertilizer use for example. Therefore, a different approach, which instead makes use of cellulose (from non-edible feedstocks) as a source of fermentable sugars, offers a promising alternative.

Cellulose is the most abundant natural polymer available on Earth and the main constituent of plant fiber. Plant fibers contain around 30-40% cellulose, with perennial biomass crops (e.g. miscanthus), arable crop residues (e.g. straws), and forestry residues (e.g. brush and sawmill residues) all abundant and low-cost sources of this polymer. However, cellulose typically exists within a complex, known as lignocellulose, alongside two other polymers: hemicellulose, and lignin. Separating and extracting cellulose from this complex, followed by subsequent processing to produce ethanol, is technologically challenging and thus, results in high capital and operational costs – making cellulosic ethanol economically uncompetitive with conventional ethanol production processes.

During cellulosic ethanol production however, there is an opportunity to also generate commercial value from the hemicellulose and lignin fractions of lignocellulose. Through valorizing these by-products there is the potential to improve the overall economic viability of this ethanol production process, thus making it more competitive. While hemicellulose can be used as an additional source of fermentable sugars for ethanol production or other chemicals, lignin is typically combusted as a process fuel which, despite offering sustainability benefits (i.e. as a renewable fuel), does not offer significant financial reward. However, by instead valorizing lignin as a feedstock for the production of polymers and chemicals, higher value products could instead be created – offering an attractive mechanism to improve the overall economics of cellulosic ethanol production.

The research presented in this report reviews and assesses the range of opportunities associated with lignin valorization in non-electricity applications, focusing on the production of: commodity and specialty chemicals, plastics, resins and composite materials.

2.1 Scope

This project reviews a variety of lignin applications developed around the globe, with specific considerations for those relevant to Indonesia (due to the potential for the establishment of a new cellulosic ethanol production facility in this region). The production of electricity from lignin combustion

is out of the scope of this review. Relevant applications do however, include (but are not restricted to) the use of lignin as a heating fuel, as a feedstock for the production of commodity and specialty chemicals, and the manufacture of plastics, resins and composite materials. This project has been divided into 3 main tasks covering:

- 1) Identification of lignin yields and technical specifications of lignin;
- 2) Review of potential applications based on lignin specifications;
- 3) Appraisal of markets associated with the applications identified.

The information presented in this report has been gathered using publicly available data and information from peer reviewed academic journals, trade publications, corporate press releases, public databases and NNFFCC's internal knowledge and contacts.

3 Lignocellulosic Biomass

Lignocellulosic biomass is an abundant and renewable resource that consists of three major components:

- 🌿 Cellulose – a polymer made up of glucose subunits;
- 🌿 Hemicellulose – a heteropolymer made up of variable C5 and C6 sugar units;
- 🌿 Lignin – a complex polymer comprised of aromatic alcohols.

Together, these components create a tough, cross-linked structure that is highly resistant to degradation. This recalcitrant matrix provides plants with structural integrity, a result of the highly crystalline nature of cellulose surrounded by supportive hemicellulose and lignin. It is this complex structure that explains why lignocellulosic biomass is notoriously difficult to breakdown into its constituent parts. This is the main economic barrier to cellulosic ethanol production at present.

Aside from applications where lignocellulose is utilized whole (e.g. as construction timber or a source of heat/power generation), this material needs to be processed in order to take advantage of the valuable components within. Biomass pretreatment is the compulsory first step towards the conversion of lignocellulose into desirable products. It involves physically or chemically disrupting the recalcitrant structure of biomass so as to make its individual fractions more susceptible to further processing. Numerous pretreatment technologies are now commercially available to aid the conversion of cellulose, hemicellulose and lignin into higher value products. However, depending on the specific pretreatment type, and indeed, the specific pretreatment conditions, the yields and specifications of isolated constituent parts can vary considerably.

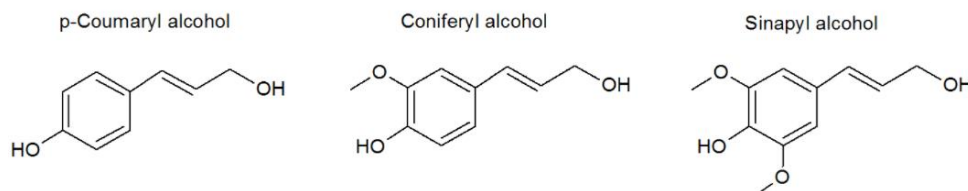
Upon reviewing the opportunities associated with the exploitation of lignin alongside cellulosic ethanol production, it is important to understand how different pretreatment technologies impact on extraction yields, purities and the properties of lignin. However, before discussing how lignin is affected by different processing methods, the following section will provide an initial overview of lignin and how it typically exists in nature prior to pretreatment.

3.1 Lignin

Lignin is the second most widely available renewable polymer found in nature (with cellulose being the most abundant) and the largest source of aromatic groups in nature. It is found within the cell walls of plants and it can account for up to 40% of dry lignocellulosic biomass by weight.² The main functions of lignin are to provide physical strength to plants, to form water-conducting vascular networks using hydrophobic interactions, and to protect plants from microorganisms and insects.³

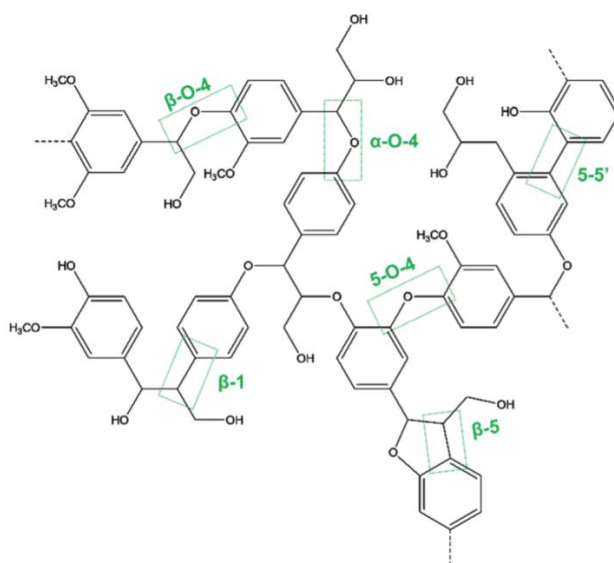
It is a highly complex material, consisting of cross-linked phenol-derived building blocks known as monolignols. The three most important monolignols contained within lignin are: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 1). These are typically incorporated into the macromolecular structure of lignin as: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units respectively.⁴ Due to the aromatic nature of lignin, it is non-fermentable and highly stable (both chemically and biologically), meaning that it contributes significantly to the strength and recalcitrance commonly associated with lignocellulosic biomass.

Figure 1: The three most prevalent monolignols found in lignin.



Unlike cellulose and hemicellulose, the exact chemical structure of native lignin is difficult to define. It tends to have a moderately high molecular weight, but the true extent of lignin polymerization is often unknown due to the fragmentation that occurs upon its extraction. In general however, lignin will be configured similarly to the structure shown in Figure 2.^{5, 6}

Figure 2: An example structure of how native lignin may be configured in nature, highlighting the most typical covalent bonds.⁷



Lignin macromolecules often contain a variety of functional groups (including hydroxy, methoxy, carbonyl, benzyl alcohol, and ether linkages for example) which are responsible for the reactive nature

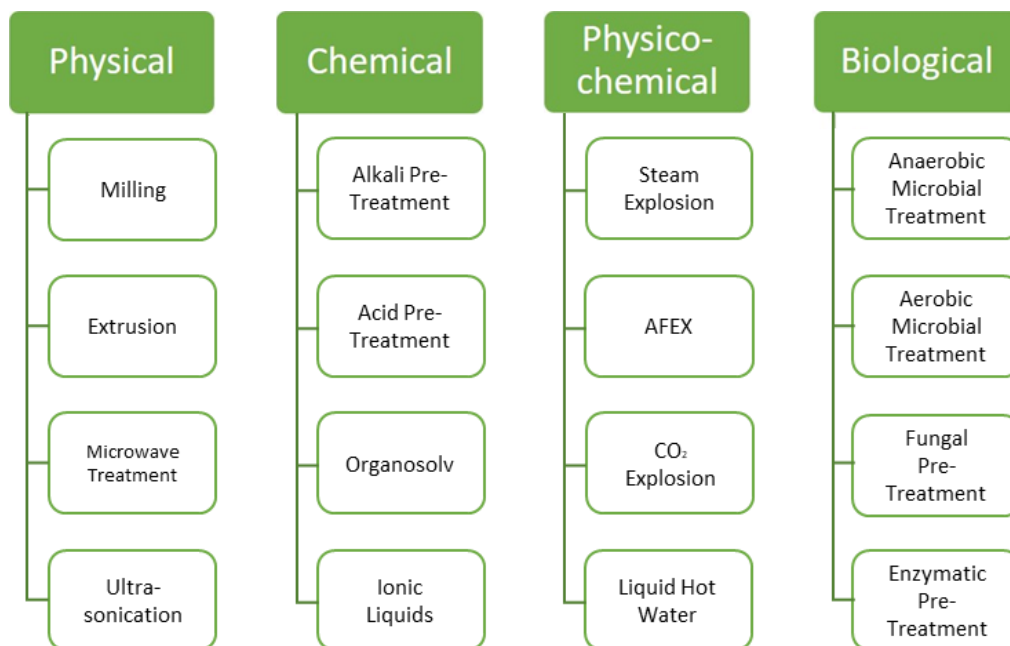
of these complexes. The presence of these functional groups is largely dependent on the ratio of monolignols contained within the biomass, which is determined by the types of feedstocks used (e.g. softwoods, hardwoods, or grasses).

Lignin composition therefore varies on the nature of the raw materials, as well as on the methods employed to process biomass. Different pretreatment processes and lignin isolation techniques will result in the generation of different types of lignin. The following chapter of this report outlines the key types of processes currently used to pretreat lignocellulosic biomass.

4 Lignocellulosic Biomass Pretreatment Technologies

There are a large and growing number of pretreatment technologies now available for the processing of lignocellulosic biomass. These methodologies can be grouped under one of four headings: physical; chemical; physico-chemical; and biological (as shown in Figure 3).

Figure 3: Different types of biomass pretreatment processes.



Physical pretreatment methods aim to reduce the particle size of the lignocellulose by breaking open its recalcitrant structure and increasing the overall surface area of the material. Larger surface areas enhance the ability of solvents and enzymes to more effectively penetrate the plant matter, resulting in improved process efficiencies downstream (i.e. further pretreatment and cellulosic ethanol production). Key physical pretreatment methods include: milling, extrusion, microwaving and ultrasonication for example. On their own however, these types of processes are ineffective at isolating the individual fractions of lignocellulose – their primary purpose is to disrupt the structure of the biomass to make it more susceptible to further processing. Physical pretreatments are therefore, generally used alongside other processing technologies or chemical extraction techniques in order to improve their overall effectiveness.⁸ Furthermore, many studies have found that the high mechanical power requirements of these processes often result in them being cost-prohibitive methods of stand-alone pretreatment during biomass to ethanol conversion.⁹

Chemical pretreatments on the other hand, involve the dissolution of biomass in a wide range of possible chemical reagents, such as: sodium hydroxide, aqueous ammonia, ammonium salts, calcium hydroxide, Lewis acids, acetic acid, formic acid, sulfuric acid, nitric acid, phosphoric acid, alkali hydrogen peroxide, sulfur dioxide, carbon dioxide, organic solvents, organic amines (propylamine, butylamine) and alcohols for example. The overall aim of these types of pretreatment technologies is to partially, or in some cases wholly, separate out the three major fractions of lignocellulosic biomass to facilitate their conversion into higher value chemicals and fuels. Key examples of chemical pretreatment processes include: acid pretreatment, alkali pretreatment, organosolv and ionic liquid processes.

Physico-chemical biomass pretreatments incorporate features of both physical and chemical processing. Whereby lignocellulosic biomass is broken down, the recalcitrant structure disturbed, and the surface area of the material increased through the use of chemicals, such as ammonia, acids, supercritical CO₂, and water. Chemicals may also then be used to separate and extract components of the lignocellulose. Pretreatment technologies that fall under this category of processes are often effective methods of fracturing biomass, and key examples include: steam explosion, ammonia fiber expansion, and liquid hot water pretreatment.

Finally, biological processes are understood to be potentially low cost and environmentally friendly methods of pretreating biomass. However, these technologies are not widely used (largely due to a lack of commercial development) and so, they will not be discussed further in this report.¹⁰

The fundamental goal of biomass pretreatment is to modify the structure of lignocellulose, whilst at the same time, where possible, removing lignin and reducing the crystallinity of cellulose. In general a successful pretreatment should:^{11, 12}

- ✦ Maximize the potential for downstream conversion into fermentable sugars;
- ✦ Minimize sugar losses;
- ✦ Maximize the potential for co-product isolation (e.g. lignin generation);
- ✦ Minimize the formation of downstream process inhibitors;
- ✦ Minimize energy use, chemical use and overall capital costs;
- ✦ Be suitable for commercial scale operation.

Preference for any particular pretreatment may vary based on the type of biomass being processed, as well as on the desired outputs of the process (i.e. cellulose, hemicellulose and lignin quality/quantities). Given **that this piece of work aims to identify opportunities associated with lignin** derived from cellulosic sugar production, the following chapter will focus on technologies specifically concerned with lignin modification and its isolation.

5 Lignin Isolation Methods

Pretreatment processes for the production of cellulosic ethanol often incorporate a combination of physical, chemical and/or physico-chemical technologies. Physical processes operate by disrupting the macromolecular structure of lignocellulose, but on their own, they are largely ineffective at isolating lignin. Therefore, they will not be discussed any further in this report.

Chemical and physico-chemical processes on the other hand, play a critical role in lignin extraction, and it is these types of technologies that typically result in different specifications and yields of lignin being generated. This section will therefore, discuss the most relevant of these processes in greater detail, and demonstrate how lignin extraction yields, as well as technical properties, vary depending on pretreatment.

5.1 Chemical Pulping Processes

Historically, the processing of lignocellulosic material has focused on the separation of single components of wood, which has given rise to the development of technologies that aim to maximize the recovery of separate constituent parts, whilst at the same time minimizing the economic costs associated with their isolation. This is exemplified by chemical pulping processes, which are designed to convert wood chips into high quality cellulose pulp for the production of paper, paperboard, textiles, and other cellulose derived products.

Chemical wood pulping began in the 19th century, the two main technologies widely used today are the Kraft process and the acid sulfite pulping process. These processes are currently the major sources of lignin available on the global marketplace, and so they are discussed in detail below to provide insight into the typical characteristics of these dominant lignin varieties. However, when it comes to cellulosic ethanol production, these pulping processes are not compatible pretreatment techniques, due to the substantial costs associated with the generation of such high grades of cellulose (these are necessary for the production of paper to provide strength and to prevent any discoloration caused by lignin, but not for bioethanol manufacturing). Given that second generation biofuels are less profitable than paper and associated products, at present it is not cost effective to employ historic chemical pulping processes for the production of cellulosic ethanol. Therefore, alternative lignin isolation methods are examined later in this section.

5.1.1 Kraft Pulping Process

The kraft process is the most widely used chemical pulping process, accounting for 90% of all chemical pulp produced around the globe (i.e. 130 million tons of pulp annually).¹³ It consists of “cooking” wood chips at 160-170°C for 2-5 hours in “white liquor” (a mixture of water, NaOH and Na₂S) at which point, over 90% of any lignin present is chemically dissolved. It is economically favored over the acid sulfite pulping process (the second most widely used chemical pulping process) due to the high recovery rates of NaOH, Na₂S (~97%) and heat.¹⁴ The major by-product of this process is referred to as “black liquor” and contains lignin, hemicellulose, and other extractives that must be removed from the wood in order to free up target cellulose fibers. This liquor contains roughly half of all the energy contained within the woody feedstocks and so, it is typically combusted in a recovery boiler, which serves as a source of steam for electricity generation and heat for the pulping process, with any excess being exported to associated industries (e.g. paper mills) or neighboring communities.¹⁵

During the pulping process, two reactions typically occur: 1) degradation reactions – where lignin macromolecules are fractured, molecular weights decrease, and lignin dissolves in the alkaline solution to create the “black liquor”; 2) condensation reactions – where lignin fragments deposit onto others, resulting in an array of higher weight molecules which can sometimes precipitate out of solution.¹⁶ Any

kraft lignin contained within the “black liquor” after pulping can be extracted by precipitation under acidic conditions – the most widely used of these processes is the commercially available LignoBoost process.¹⁷ Acidification is typically carried out in two steps, the first uses CO₂ to reduce the pH of the liquor to around pH 9-10. When black liquor is acidified, the phenoxide groups present in dissolved lignins become protonated and lignin solubility decreases. Around three quarters of the lignin present in the liquor is precipitated and collected during this step.¹⁸ In the second stage, the pH of the solution is lowered further to <pH 3 with H₂SO₄ and the remaining lignin is filtered out. Both precipitates are collected together and washed several times with water to eliminate impurities.¹⁹ The resulting lignin is then recognized as a highly pure product.ⁱ

However, a major problem that has been identified with the LignoBoost process, and other technologies that purify kraft lignins using sulfuric acid, are that they increase the elemental sulfur content of lignin. This creates an odor, and it has been seen as an obstacle in producing different consumer products from kraft lignin. Especially when making composites (such as plastics, binders or coatings), as final products, despite being manufactured using pure lignin, can still have a characteristic smell. The general perception is that sulfurous compounds are to blame for this smell and that sulfur free lignins are generally odor free lignins.²⁰ Sulfur-free lignins are more versatile and can be heat-treated without the release of foul-smelling sulfur compounds.

Hardwood, softwood, and fibrous non-wood biomass can be used as feedstocks in the kraft process. Kraft lignin, even if derived from a variety of different raw materials, however, often presents common features that are inherent to the process’s conditions. These types of lignins typically: contain large numbers of phenol groups, a result of the extensive cleavage of β-O-4 ether bonds during the pulping process; they form a range of condensation structures due to the intense conditions used during cooking; they usually contain around 2–3% total sulfur due to reaction with Na₂S; and in some cases, they form catechol and carboxyl structures due to the highly oxidative conditions employed during delignification. Furthermore, the extensive cleavage of β-O-4 ether bonds during pulping, often results in fractions of purified lignin that subsequently demonstrate relatively low number-averaged molecular weights (Mn), in the region of around 1000–3000 Da.^{21, 22} The molecular weight range of kraft lignin however, can vary from around 600 Da to over 180,000 Da due to the varying degree of polymerization during processing.^{23, ii} This results in a low degree of homogeneity (i.e. high polydispersity) across kraft lignin samples and is therefore indicative of a poor quality, inconsistent product – a key limitation when looking to use this type of lignin in value-added applications.

Furthermore, kraft lignin is soluble only in basic solutions and in highly polar organic solvents – it does not dissolve in water, which limits its potential in many industrial applications. In order to increase the commercial opportunities available to this type of lignin, it can therefore be chemically modified so that it can then be used as a starting material for the production of polymers and chemicals. However, such modifications are challenging due to the structural complexity and heterogeneity of kraft lignin, and the most reactive sites present within these structures are often sterically hindered or occupied by

ⁱ) High purity in this sense corresponds to lignin products that are largely free from common contaminants (such as carbohydrates, ash, metals/elements, and extractives) that enter lignin product streams through pulping and pretreatment processes.

ⁱⁱ) Mn = number-averaged MW. Mw = weight-averaged MW. Mn reflects the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample. Mw depends not only on the number of molecules present, but also on the weight of each molecule (i.e. it is a weighted average). Mn is the main measure of MW to be quoted in this report as it is less influenced by the skew of particularly high/low weight fragments of lignin in a given sample.

interconnecting bonds. This demonstrates that kraft lignin is relatively inert, in the sense that it is difficult to modify and use in value-added applications – it is not an ideal feedstock for the manufacture of valuable chemicals and so, it is primarily used as a biofuel for energy generation.

The most notable company to have developed a commercial process for the conversion of kraft lignin into higher quality, water soluble products is Ingevity, the specialty chemicals division of WestRock (formally MeadWestvaco). They manufacture high-purity, 'kraft lignosulfonates' (as demonstrated by their AltaBio, Hyact, Kraftplex, Kraftspere, Polyfon and Reax range of products)²⁴ that are typically produced by sulfonating kraft lignin in the presence of an aldehyde (such as formaldehyde) and sodium sulfite or sodium bisulfite for example. These highly modified kraft lignin products are largely marketed as dispersants for use in a range of end-use sectors.

In summary, the key features of (unmodified) kraft lignins are:

- ✦ High lignin yield ~ 90% recovery from biomass;
- ✦ Low-number average molecular weight (Mn);
- ✦ High polydispersity;
- ✦ Large number of condensation and derivatized products;;
- ✦ Highly pure product following isolation/purification;
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.1.2 Acid Sulfite Pulping Process

In terms of pulp and paper production, the acid sulfite pulping process is much less widely used than the aforementioned kraft pulping process. However, the lignin outputs generated by this process (also known as lignosulfonates) can be used in a much wider range of downstream applications due to the presence of favorable functional groups that result in them being soluble in water. Lignosulfonates account for roughly 90% of all commercial lignin produced annually, corresponding to a worldwide production volume of approximately 1.8 million tons.²⁵ The world's leading manufacturer of this type of lignin is Borregaard LignoTech, based out of Norway. They are believed to produce approximately 40% of all the lignosulfonates manufactured around the globe.²⁶

This pulping process works by dissolving lignin at 140-160°C in the presence of sulfite salts (e.g. SO_2 , HSO_3^- , or SO_3^{2-} combined with either Na, Ca, NH_4 or Mg). It is believed that upwards of 95% of the lignin contained within biomass can be removed by this pulping process.²⁷ However, it does not selectively remove this lignin since carbohydrates contained within the lignocellulose (particularly hemicellulose) are also solubilized during the process. As a result, the "brown liquor" generated during the cooking of feedstocks is known to include a high volume of residual sugars, as well as sugar dehydration products, inorganics, and acid derivatives (e.g. acetic acid). Several purification steps are therefore required in order to obtain lignosulfonates of a sufficient quality to use in downstream applications. Direct precipitation of these lignin varieties in acidic media followed by filtration is not possible for spent sulfite liquors (as is the case for "black liquor" and the isolation of kraft lignin) as lignosulfonates are highly soluble across the entire pH-range and therefore will not precipitate out of solution. Alternative methods of purification are thus employed (e.g. fermentation to convert sugars into ethanol, membrane separation and ultrafiltration).²⁸ Isolated lignosulfonates can therefore demonstrate lower purities than kraft lignins due to the fact that they are generally more difficult to refine. A typical lignosulfonate lignin fraction can contain up to 30% impurities by weight.²⁹

The acid sulfite pulping process is less common than the kraft process due to the reduced range of feedstocks that are compatible with this technology (i.e. not suitable for woody biomass that contain resins, such as Douglas fir or pine for example),³⁰ the cost of reducing process emissions is higher, and it is difficult to recover and recycle the initial chemical inputs of the process (i.e. sulfite salts), which makes it less economical overall.³¹ It does however, result in the production of water-soluble lignosulfonates that can be used in a much wider array of downstream applications compared to kraft lignin. During this pulping process, the main reactions that occur are acid hydrolysis and sulfonation – they involve the loss of hydroxyl groups and the cleavage of ether bonds followed by the bonding of lignin fragments with sulfur groups, resulting in a high degree of sulfonated sites. Lignosulfonates are believed to contain approximately 5-8wt% of sulfur,³² and it is the presence of these groups which gives lignosulfonates their water solubility (due to the way that they interact with water molecules). According to Borregaard, at least one in every four C9 units needs to be sulfonated in order for the lignin to be water soluble.³³ It is this high degree of sulfonation which means that lignosulfonates are suitable for a wide range of applications downstream, and as a result there has also been commercial interest in sulfonating kraft lignin (as discussed in the previous section) to allow kraft paper producers to benefit from these commercial opportunities.

Lignosulfonates are generally less depolymerized than kraft lignins (due to fewer ether bonds undergoing cleavage during pulping) which results in higher average molecular weight materials (i.e. 20,000-50,000 Da on average). Furthermore, the addition of sulfonate groups during the acid sulfite process is also believed to contribute to the high molecular weights of lignin fragments. However, the exact number-average molecular weight of lignin will typically vary depending on the raw material processed, with hardwood lignosulfonates exhibiting lower molecular weights (5,700-12,000 Da) compared to softwood lignosulfonates (36,000-61,000 Da).^{34, 35} In terms of molecular weight distribution, lignosulfonates are known to demonstrate high polydispersities, as pulping conditions can cause a range of condensation and degradation products to form,³⁶ which further highlights a need for efficient purification processes following pulping.

As the world's leading manufacturer of lignosulfonates, Borregaard, have also developed the BALI (**B**orregaard **A**dvanced **L**ignin) technology, which is based on acid sulfite pulping for the production of water soluble performance lignins, as well as cellulosic sugars for ethanol manufacturing. This process is unique in that alternative pretreatments employed prior to cellulosic ethanol production (discussed in the following section) do not yield water soluble lignins. Therefore, this is an important development to highlight in terms of the potential to generate lignosulfonates alongside cellulosic ethanol. A demonstration plant has been in operation since January 2013, and Borregaard have stated that their "technology is ready for scale up when the market is ready".³⁷ However there have been no announcements of plans for the scale up of production as of yet.

In summary, the key features of lignosulfonates are:

- 🌱 High lignin yield ~ 95% recovery from biomass;
- 🌱 High-number average molecular weight (Mn);
- 🌱 Large distribution of Mw (i.e. heterogenous/high polydispersity);
- 🌱 Large number of condensation and derivative products (i.e. low purity);
- 🌱 Water soluble.

5.2 Pretreatment Technologies

Despite being the key sources of lignin generation at present, the aforementioned pulping processes are not compatible pretreatment methods for the production of cellulosic ethanol, due to the substantial costs associated with the generation of high grade cellulose. Second generation biofuels are less profitable than paper and associated products, and so it is not currently cost effective to employ chemical pulping processes for the production of cellulosic ethanol. The remainder of this chapter will therefore evaluate a variety of biomass pretreatment technologies that can be used prior to the production of cellulosic ethanol, as a means of isolating lignin.

5.2.1 Alkali Pretreatment

There are various technologies available for the pretreatment of lignocellulosic biomass, and those that utilize alkalis as a means of delignification have emerged as some of the most favorable processes, as they are able to demonstrate a number of desirable features. For example, alkali pretreatments largely utilize non-polluting and non-corrosive chemicals (e.g. ammonia, sodium hydroxide, sodium carbonate, and lime); they are typically carried out under milder conditions than those needed for acid pretreatments for example; and alkaline reagents interact primarily with the lignin components of lignocellulose, meaning that they are effective technologies for the delignification of biomass.³⁸

The exact conditions required for pretreatment largely depend on the alkalis used during the process. For example, when sodium hydroxide (NaOH) or sodium carbonate (Na₂CO₃) is used, a temperature between 60–180°C is commonly required with a treatment time of around 5–60 min. The use of NaOH will typically lead to around 60–80% delignification, whereas Na₂CO₃ typically results in around 40–60% of the lignin being removed. Although Na₂CO₃ has a lower delignification efficiency than NaOH, it is less expensive and is easier to recover at the back-end of the process. Ammonia pretreatment on the other hand is known to achieve lignin yields upwards of 80%, but high temperatures (between 150–210°C) and pressure are typically required for around 5–60 min. The use of lime as an alkaline reagent however, requires much lower temperatures (25–130°C) over a period of a few hours to potentially a number of weeks.³⁹ Despite lime pretreatment requiring extended processing times, it is a simple, low cost and low energy procedure that results in approximately 60–80% delignification.⁴⁰ By increasing the temperature of alkali pretreatment processes, delignification can be accelerated. However, more severe pretreatment conditions can lead to the production of lignin condensation products, which can impact on the weight distribution of lignin molecules present within a generated sample.⁴¹ In ammonia recycle percolation (ARP) systems (where ammonia is the alkali used for the pretreatment of biomass), the re-polymerization and re-precipitation of soluble lignin onto the surface of biomass is minimized as soluble lignin is discharged from the reactor as soon as it is formed.⁴² This is an example of how these side reactions can be avoided.

In general, alkaline pretreatment is more effective on hardwoods, grasses and agricultural residues, which have lower lignin contents, than softwoods.^{43,44,45} The major reactions that occur during these processes include the cleavage of ether bonds for the dissolution of lignin and the formation of highly phenolic products. In a way, these lignin varieties are similar to kraft lignin, but the severe process conditions of the kraft process allows for more efficient cleavage of β -O-4 ether linkages to take place, which results in lower molecular weight fragments. Alkali lignins therefore exhibit higher molecular

weights than kraft lignins – in the region of 4,000-6,000 Da.^{46,47} Of those β -O-4 ether linkages that do cleave however, more stable bonds are generally formed in their place – leading to less reactive lignin molecules. They are also not water soluble which can limit their range of applications.

In summary, the key features of alkali-derived lignins are:

- ✦ Variable lignin yield ~60-80% recovery from biomass;
- ✦ Relatively high-number average molecular weight (M_n);
- ✦ High polydispersity;
- ✦ Large number of condensation/side products generated;
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.2 Dilute Acid Pretreatment

An alternative group of biomass pretreatment processes operate by instead using acids to fractionate lignocellulose. They can be separated into dilute acid and concentrated acid treatment methods, and unlike alkali pretreatments, they do not selectively target the lignin components of lignocellulose – but work by targeting the carbohydrate components.

Dilute acid processes are currently the most widely used commercial pretreatment methods for the disruption of lignocellulose. The most common types of acids used with these technologies are, dilute sulfuric acid (H_2SO_4), dilute nitric acid (HNO_3), phosphoric acid (H_3PO_4), and dilute hydrochloric acid (HCl).⁴⁸ Acid is usually sprayed onto biomass, or agitated with biomass in a reactor, and one of two process conditions are typically used:^{49,50}

- 1) A high-temperature ($>160^\circ C$), continuous-flow process for low solids loadings (5-10%); or
- 2) A low-temperature ($<160^\circ C$), batch process for high solids loadings (10-40%).

The most tried and tested approaches tend to be based on the use of dilute H_2SO_4 and dilute H_3PO_4 since they are relatively cheap and efficient at hydrolyzing lignocellulose (though the latter gives a milder effect and is more benign to the environment).⁵¹ The process results in the hydrolysis and solubilization of hemicellulose, and the breaking of ether bonds in lignin (such as β -O-4 linkages), leading to lignin depolymerization. Continuous flow-processes tend to be much more effective at lignin removal (~60%), whereas batch processes often result in much lower lignin yields (~20%).^{52, 53} Lignin fragments are largely hydrophobic and so they do not dissolve well in acidic, aqueous media. Dilute acid pretreated lignin is therefore, known to coalesce into aggregates and relocate on the surface of the biomass where it can be recovered as insoluble residues.^{54, 55} A small part of the lignin however, is able to be solubilized (around 5–10% of total lignin) and this can be recovered as acid soluble lignin.⁵⁶

During dilute acid hydrolysis, acids catalyze the breaking of ether bonds (such as β -O-4 linkages) which leads to lignin depolymerization. In terms of the resultant molecular structures, it is believed that lignins derived from dilute acid pretreatment processes will exhibit molecular weights in the range of around 20,000-25,000 Da. This can be attributed to the fact that dilute acids do not depolymerize lignins as extensively as other pulping/pretreatment processes discussed.

Dilute acid hydrolysis also has a number of limitations. The corrosive nature of acids means that expensive construction materials are required to limit the effect of corrosion over time, and acids need

to be neutralized and recovered which adds to overall operating costs. Furthermore, dilute acid pretreatments often generate by-products such as humins, which can inhibit yeasts and other microorganisms (which may negatively impact downstream processing). The acids themselves are also toxic to yeasts, and so fermentation yields can be inhibited during the production of cellulosic ethanol, unless cellulose pulps are washed extensively.

In summary, the key features of dilute acid-derived lignins are:

- ✦ Variably low lignin yields 20-60% recovery from biomass;
- ✦ Relatively high-number average molecular weight (Mn);
- ✦ High polydispersity;
- ✦ Large number of condensation and derivatized products;
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.3 Concentrated Acid Pretreatment

Concentrated acid hydrolysis much like dilute acid pretreatment, targets the carbohydrate fractions of lignocellulosic biomass. However, in these cases, both the cellulose and hemicellulose fractions of biomass are solubilized, allowing for their extraction from the biomass. H_2SO_4 is the most widely used acid in these pretreatment processes. In a first step, feedstocks are incubated at $\sim 40^\circ C$ in 70% acid for around 2-6 hours. Water is then added, and several rinse steps are used to recover the solubilized sugars. The solid that remains after this first stage is dewatered, and then soaked in 30-40% acid for 1-4 hours. Sugars are separated using ion exchange resins, and the remaining acid is recycled. This process operates by increasing the accessible surface area of the biomass, it hydrolyses cellulose and hemicellulose, and alters lignin structure.

It works in a similar way to the previously discussed dilute acid pretreatment process i.e. it does not specifically delignify the biomass (as lignin is not fully soluble in aqueous, acidic media). However, given that concentrated acids are able to solubilize both cellulose and hemicellulose, this allows for a higher yield of lignin to be separated and recovered compared to dilute acid pretreatment processes (i.e. $>60\%$). Furthermore, the use of strong acids results in a higher degree of labile bonds undergoing cleavage – causing lower molecular weight fragments of lignin to form (i.e. $<20,000$ Da), and a reduction in the overall reactivity of these compounds. Strong acids also result in the generation of a higher degree of condensation products - which can lead to wide range of molecular weight products forming (unless processing takes places at low temperatures).

Concentrated acid hydrolysis can be used with a wide range of different feedstocks, but the recycling of acids is essential for the economic viability of the process, and equipment corrosion can be a problem, as can the production of toxic degradation products, which can affect downstream processes.

In summary, the key features of concentrated acid-derived lignins are:

- ✦ Modest lignin yield $>60\%$ recovery from biomass;
- ✦ Relatively low number average molecular weight (Mn);
- ✦ High polydispersity;
- ✦ Large number of condensation and derivatized side products;
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.4 Liquid Hot Water Pretreatment

Liquid hot water (or hot liquid autohydrolysis) is a physical treatment which uses liquid phase water at high temperatures and pressures (~5 MPa and 180-230°C for ~15 minutes).⁵⁷ The process removes hemicellulose together with some lignin, and the pH of the pretreatment liquor can be controlled through the addition of a base (e.g. potassium hydroxide). Maintaining a pH between 5 and 7 minimizes the hydrolysis of hemicelluloses to monosaccharides, and thus limits the production of fermentation inhibitors when this pretreatment method is used.^{58,59}

This pretreatment method is mainly targeted at hardwoods and softwoods,⁶⁰ and it aims to solubilize hemicellulose to improve the subsequent processability of the biomass. Lignin is primarily recovered as an insoluble residue (as is the case for acid hydrolysis pretreatments) and so the solid fraction must be separated in order to isolate lignin.⁶¹ This method enhances the breakdown of cellulose without having to handle acids, and without the need for significantly reducing the size of biomass prior to processing. Although the generation of sugar degradation products is observed when using liquid hot water pretreatments (which can potentially lead to the inhibition of downstream processing), the low residence times employed by these processes, in fact, limits their formation.

The yields of lignin generated by these pretreatment processes are known to be relatively low (around 60% for example),⁶² and in terms of lignin properties, they are believed to demonstrate relatively low molecular weights in the region of around 5000-10,000 Da. This is presumably a result of the high temperatures and pressures involved in the process, which likely plays a role in the cleavage of lignin bonds to generate smaller molecules.

Liquid hot water pretreatments are attractive from a cost saving point of view, as no chemicals or corrosive materials are used. Furthermore, the opportunity for recovering pentoses is high, and the action of forming inhibitory products is relatively low (when compared to other types of pretreatments discussed in this study). However, in terms of disadvantages, a high amount of water and energy are required in order to carry out this process, and lignin removal is not particularly effective.⁶³

In summary, the key features of liquid hot water-derived lignins are:

- ✔ Modest lignin yield ~60% recovery from biomass;
- ✔ Relatively low-number average molecular weight (Mn);
- ✔ High polydispersity;
- ✔ Fewer condensation/side products generated than other pretreatment processes;
- ✔ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.5 Steam Explosion

Steam explosion involves subjecting biomass to steam at high temperatures (160-260°C) and pressures (20-50 bar), followed by rapid decompression to atmospheric levels in order to terminate the reaction. This causes an 'explosion' within the biomass, and leads to cell wall disruption. Steam explosion results in a rearrangement of lignocellulose, which increases the surface area of the material - lignin is partially removed during this process and redistributed on the surface of the biomass. A wash step is then employed to remove any breakdown products that arise from this process. For example, alkali washing or the use of organic solvents allows for the recovery of hardwood lignins in yields of up to 90%.⁶⁴ Lignin

fractions resulting from this process subsequently demonstrate low molecular weights (i.e. 1000-2500 Da).⁶⁵

Steam explosion is believed to be more effective for hardwoods than for softwoods, and the use of acids to catalyze this process is often considered a pre-requisite for softwoods. Such catalysts may include H₂SO₄ or SO₂ (with gaseous SO₂ able to reduce the corrosion issues often observed with the use of H₂SO₄).

In summary, the key features of concentrated steam explosion-derived lignins are:

- ✦ High lignin yield after washing with alkali or organic solvent (i.e. ~90% lignin removal);
- ✦ Low-number average molecular weight (M_n);
- ✦ High polydispersity;
- ✦ Large number of condensation and derivatized products;
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.6 Ammonia Fiber Expansion (AFEX)

Ammonia fiber expansion (AFEX) is a physicochemical process that is similar to steam explosion. However, unlike steam explosion, this pretreatment technology has not yet been commercialized. AFEX works by exposing lignocellulosic biomass to ammonia at high temperatures (60-110°C) and pressures for 30 minutes or less,⁶⁶ and a sudden pressure release results in the physical disruption of cell walls, exposing biomass fibers. Ammonia can then be easily recycled by evaporation, which reduces waste, as well as the costs associated with its replacement. There is little to no loss of biomass when using this method – i.e. it does not remove lignin or any other substance from lignocellulose. It is a dry-to-dry process and employs no washing step, therefore it is particularly challenging to recover lignin from this type of pretreatment (unless coupled with further processing).⁶⁷ As such, there is limited data available on the specifications of AFEX lignin varieties.

AFEX results in the physical rearrangement of biomass, including the cleavage of lignin-hemicellulose bonds. This process operates at much lower temperatures and pressures than steam explosion, but it requires higher biomass loadings (i.e. 60-90% solids).⁶⁸ It is known to be less effective when used with materials that have a high-lignin content – i.e. it works best with herbaceous biomass and agricultural residues, and it works moderately well on hardwoods (it is less effective on softwoods).⁶⁹

Limited data is available on the specifications of AFEX lignin, however the following is assumed:

- ✦ Low lignin yields;
- ✦ Relatively high-number average molecular weight (M_n);
- ✦ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.2.7 Organosolv Pretreatment

Organosolv processes use mixtures of water and organic solvents and acids to fractionate biomass.^{70,71,72} Much like the kraft process and the acid sulfite process, the origins of organosolv also stem from the pulp and paper industry. It was initially developed as an environmentally friendly alternative to kraft and sulfite pulping, that can be operated at lower scales.⁷³ However, although organosolv has been known in the pulping industry for decades, it has not yet been commercialized, due to its unfavorable

economics.⁷⁴ The development of markets for both hemicellulose and lignin will therefore, be a key requirement when looking to scale up this category of pretreatment technologies in the future.

The organosolv process refers to the heating of biomass in an organic solvent (such as ethanol) and water, at high temperatures (150-200°C) and pressures for around 30-60 minutes, using a catalyst such as H₂SO₄ (or more rarely NaOH).⁷⁵ Technologies are typically aimed at the delignification of biomass i.e. the hemicellulose fraction of the biomass is hydrolyzed, and the lignin removed. There are a range of different organosolv varieties, but the best known technology is the Alcell pulping process which uses ethanol, or a 1:1 ethanol-water mixture.⁷⁶ Biomass chips are cooked in this pulping solution at ~195°C for an hour. No acid or alkali is added but the release of acetic acid from acetyl groups in the biomass maintains a pH of around 4. The outputs of this process are cellulose pulp (or Alcell pulp), low molecular weight lignin, hemicellulose saccharides, furfural and acetic acid.

Around 70-90% of lignin is recoverable using organosolv processes. Lignin is precipitated from the liquor and dried for sale, and the number-average molecular weights of these lignins are typically around 1000 Da.⁷⁷ Most organosolv lignin is insoluble in acidic aqueous solutions, but will dissolve in basic solutions, and in most polar organic solvents. These types of lignins demonstrate very high purities, with low contamination from sugar degradation products.

In summary, the key features of organosolv lignins are:

- ✔ High lignin yield ~ 70-90% recovery from biomass;
- ✔ Low-number average molecular weight (Mn);
- ✔ Furfural and acetic acid generated;
- ✔ Highly pure product following isolation/purification;
- ✔ Only soluble in basic solutions and highly polar organic solvents (i.e. hydrophobic).

5.3 Summary of Biomass Pretreatment Technologies

At present, the majority of lignin produced around the globe originates from either an acid sulfite or a kraft pulping process. The latter, although the most dominant process used for the pulping of wood worldwide, generates lignins that are known to have less commercial applications compared to lignosulfonates formed as a result of the acid sulfite pulping process. Lignosulfonates are high molecular weight, water soluble chemicals that account for roughly 90% of all commercial lignins generated annually. Kraft lignins on the other hand, are low molecular weight compounds that are not soluble in water. Lignosulfonates are also more reactive than kraft lignins, due to the partially preserved β -O-4 linkages present in these compounds (in comparison, these bonds are extensively cleaved during the kraft process, on account of the harsh pulping conditions employed) – this makes them more susceptible to chemical modification downstream, allowing them to be prepared for use in a range of different types of applications (i.e. surfactant manufacturing, chemical synthesis, polymer production etc.).

When it comes to cellulosic ethanol production however, neither the kraft nor the acid sulfite pulping processes are compatible pretreatment techniques, due to the substantial costs associated with the generation of high quality cellulose for paper and card manufacturing. Alternative pretreatment technologies include: alkali, dilute acid, concentrated acid, liquid hot water, steam explosion, AFEX, and

organosolv processes. All of these technologies, with the exception of concentrated acid, AFEX and organosolv, are currently commercially available for the pretreatment of lignocellulosic biomass.

In terms of lignin recovery, steam explosion, organosolv, and alkaline pretreatments demonstrate the highest attainable yields. Followed by concentrated acid, dilute acid, and liquid hot water pretreatments. AFEX however, does not generate extractable lignin in sufficient quantities for it to be considered a suitable pretreatment method for lignin valorization.

These pretreatment technologies also generate a wide range of molecular weight lignins – those that produce high molecular weight fractions include dilute acid, concentrated acid and AFEX pretreatments, and those that produce low molecular weight fractions include alkaline, liquid hot water, steam explosion and organosolv pretreatments. In general, all lignin fractions display a high number of phenol and hydroxyl groups, and the presence of β -O-4 linkages and other labile bonds tends to correspond with the degree of lignin depolymerization i.e. smaller lignin fragments generally contain less of these reactive sites as they have been more extensively degraded. High molecular weight lignins therefore, tend to be more reactive than low molecular weight compounds.

In general, it can be said that all pretreatment technologies yield relatively impure lignins, with the exception of organosolv. Furthermore, no pretreatment technologies available at present are able to generate water soluble lignins that are comparable to lignosulfonates (with the exception of Borregaard's BALI process which is based on acid sulfite pulping technology). This is significant, as it means that no lignins obtained by current pretreatment processes will be suitable for applications that require water solubility, unless of course additional modification processes are carried out (as has been demonstrated for kraft lignins).

Finally, with regards to the types of biomass feedstocks that can be used with each of these processes, in general, all are equipped to accept agricultural residues (Table 1). Therefore, when considering the types of feedstocks that are readily available in Indonesia (e.g. rice/maize straw, oil palm empty fruit bunches, sugarcane residues and bagasse etc.),⁷⁸ all technologies could be potentially used as a means of pretreatment prior to cellulosic ethanol production. Furthermore, all processes aside from acid sulfite pulping process and the AFEX process are able to effectively process hardwood feedstocks.

Table 1: The compatibility of different feedstock types with each pulping/pretreatment process.

Lignin Isolation Method	Softwood	Hardwood	Agricultural Residues
Kraft Pulping Process	✓	✓	✓
Acid Sulfite Pulping Process	✓	X	✓
Alkaline Pretreatment	X	✓	✓
Dilute Acid	X	✓	✓
Conc Acid	X	✓	✓
Liquid Hot Water	✓	✓	✓
Steam Explosion	X	✓	✓
AFEX	X	X	✓
Organosolv	X	✓	✓

Table 2: Summary of the most notable pulping processes and biomass pretreatment technologies, and the properties of lignins that result from each one.

Lignin Isolation Method	TRL ⁱⁱⁱ	Lignin Yield	Process Mechanism	Lignin Properties			
				Average MW (Mn) (Da)	Purity	Notable Functional Groups	Solubility
Kraft Pulping Process	9	~ 90%	Lignin dissolved in aqueous solution of NaOH and Na ₂ S.	1,000 - 3,000	Moderate	Large number of phenol groups. 2-3% sulfur content. Extensive degradation of β-O-4 ether bonds.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Acid Sulfite Pulping Process	9	~95%	Dissolve lignin and hemicelluloses using sulfites.	20,000 - 50,000	Low	High degree of sulfonation (4-8% sulfur content). Partial preservation of β-O-4 linkages.	<ul style="list-style-type: none"> • water • non-organic solvents
Alkaline Pretreatment	9	60-80%	Lignin dissolved in alkaline reagents.	4,000-6,000	Moderate	High number of phenol groups. Free from S. N incorporation when ammonia used. Degradation of β-O-4 ether bonds.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Dilute Acid	9	20-60%	Hemicellulose dissolved in dilute acids. Lignin depolymerized and removed.	20,000-25,000	Moderate/ Low	High number of phenol groups. Partial preservation of β-O-4 linkages.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Conc Acid	6	>60%	Hemicellulose and cellulose dissolved in concentrated acids. Lignin depolymerized and removed.	<20,000	Moderate/ Low	High number of phenol groups. Partial preservation of β-O-4 linkages.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Liquid Hot Water	9	~60%	High temperature and pressure water used to solubilize hemicellulose and lignin.	5,000-10,000	Moderate	High number of phenol groups. Partial preservation of β-O-4 linkages.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Steam Explosion	9	~90%	High temperature and pressure water used to depolymerize hemicellulose and lignin. Washed with alkali or organic solvent,	1,000-2,500	Moderate/ Low	High number of phenol groups. Degradation of β-O-4 ether bonds.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
AFEX	5	Low	High temperature and pressure ammonia used to fracture biomass.	High	Moderate/ Low	Partial preservation of β-O-4 linkages.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents
Organosolv	5	70-90%	Organic solvents (e.g. ethanol) used to hydrolyze hemicellulose and solubilize lignin	1,000	High	Large number of phenol groups. Sulfur free lignin Extensive degradation of β-O-4 ether bonds.	<ul style="list-style-type: none"> • basic solutions • highly polar solvents

ⁱⁱⁱ) See Annex I for more information on Technology Readiness Levels (TRLs)

6 Lignin Applications

Having reviewed a variety of biomass pretreatment options for the production of cellulosic ethanol, and outlined the yields and specifications of lignin that result from each one, the following section will now review the range of possible applications available to these lignins, based on recent industry developments.

At present, the majority of applications currently available to lignin are based around the use of lignosulfonates and kraft lignins (i.e. the most readily accessible lignins found on the market). However, as has been demonstrated, a variety of other lignin types can be obtained from the pretreatment of feedstocks prior to cellulosic ethanol manufacturing, and these can vary in terms of the properties that they exhibit – potentially making them more or less suitable for use in certain applications.

This section therefore discusses some of the most important applications currently associated with lignin, and outlines the specific characteristics that makes them suitable for use in these roles. These will be discussed in order of their potential value on the market – i.e. whether they are considered high, medium, or low-value applications. A comprehensive overview of each application is provided, and consideration is given to: how and where lignin is used; the technology readiness of developments in each area; and the expected timeline for commercialization, whilst recognizing the likely barriers to market uptake.

6.1 High-Value Market Applications of Lignin

High-value specialised applications typically represent a small segment of lignin's total market – believed to cumulatively correspond to just 10% of lignin consumption by volume. Lignin products classified as “high-value” would typically expect to command a market price upwards of \$750 per ton.⁷⁹ The most commercially interesting of these applications are discussed below.

6.1.1 Aromatic Chemical Production

Given the highly aromatic nature of lignin, this abundant resource is therefore an excellent source of aromatic chemicals. A considerable volume of research has been carried out into the production of various compounds from lignin, however, only one has been successfully commercialized to date. Vanillin is not only one of the most well-known uses of lignin, it is also one of the only phenolic compounds to be manufactured from biomass on an industrial scale. Around 20,000 tons of vanillin are produced in total every year, and around 15% comes from lignin (approximately 3,000 tons).⁸⁰ Vanillin can be used in a range of downstream applications, including in:

- ✿ Flavors;
- ✿ Fragrances; and
- ✿ Pharmaceuticals.

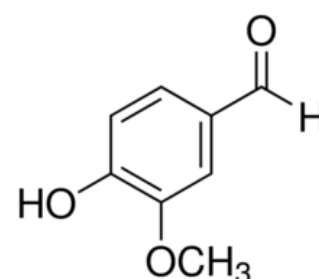


Figure 4: Chemical structure of vanillin.

The production of vanillin from lignin originates from the use of lignosulfonates (derived from acid sulfite pulping liquors) and manufacturing began in North America in the 1930s. This was one of the main methods of generating synthetic vanillin until the end of the 1990's, when almost all lignin-to-vanillin plants closed. This was primarily due to the increase in availability of inexpensive chemical intermediates arising from fossil fuels – meaning that vanillin synthesis from lignin became economically uncompetitive. The majority of vanillin currently available on the market is now derived from petroleum.⁸¹

The process for producing vanillin consists of treating an aqueous solution of lignin (i.e. lignosulfonates) with oxidants at an alkaline pH, and at high temperatures and pressures, in order to depolymerize lignin macromolecules and to obtain vanillin. A major challenge when depolymerizing lignin into value added-compounds (i.e. other lignin-derived chemicals, not just vanillin) is the requirement for selectively cleaving bonds within the lignin macromolecular structure. While native lignin is highly reactive towards depolymerization, lignin streams isolated from pulping processes or biomass pretreatment processes are typically more recalcitrant – a result of the structural condensation and/or degradation that occurs during biorefining. Structural degradation involves cleaving reactive ether and ester linkages, and forming stable carbon-carbon bonds *via* condensation reactions. Therefore, lignin streams that contain a higher degree of preserved ether and ester bonds (particularly reactive β -O-4 linkages) are typically more susceptible to depolymerization, and they are therefore considered more effective starting materials for the production of vanillin (as well as other downstream chemical compounds).⁸² Research indicates that the more β -O-4 linkages present in lignin, the higher the yield of corresponding aldehydes produced (e.g. vanillin) – it is believed that vanillin yields can therefore be enhanced by using lignin streams with high β -O-4 contents.⁸³ This is why lignosulfonates are used rather than kraft lignins for the production of vanillin. Furthermore, it is believed that lower molecular weight lignosulfonates generate better results when manufacturing vanillin,⁸⁴ presumably because fewer bonds need to be cleaved during the oxidative depolymerization of smaller lignin fragments.

With regards to the commercial development of this application, the key player involved in production of vanillin from lignin is the Norwegian company, Borregaard. They have been running a lignin-to-vanillin plant in Sarpsborg, Norway for more than 50 years, and for the last 20 years, have been the only operator of this process. Borregaard therefore exists as the only producer of vanillin from wood at present⁸⁵ - and use lignosulfonate lignins as their starting material.

Given that the production of vanillin from lignin is a commercially developed process, this application has therefore reached a technology readiness level (TRL) of 9. The main barrier to further development and growth in this area however, is believed to be the costs associated with using lignosulfonate lignins compared to fossil-derived starting materials. Nevertheless, there is still notable demand for vanillin from lignin, as it allows consumers to opt for a more environmentally friendly and renewable product over an oil-derived alternative. At present, the main route for the production of vanillin from lignin is based upon the use of aqueous (i.e. water soluble) lignosulfonates, primarily because they are more reactive than kraft lignins. Nevertheless, this does mean that the main synthesis route is based around an aqueous environment, and so it would not be feasible to instead use insoluble lignins in the place of lignosulfonates (unless they undergo additional processes modification prior to their use).

The key features of lignin used by the existing commercial route to vanillin include:

- 🌿 High degree of ether and ester bonds present;
- 🌿 High purity lignin;
- 🌿 Low molecular weight;
- 🌿 Water soluble.

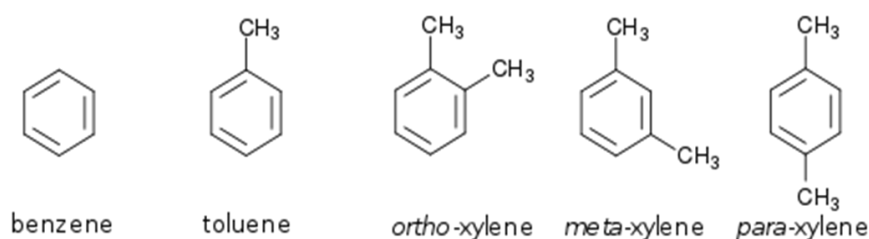
Although vanillin is currently the only compound made from lignin on a commercial scale, there are a diverse range of other aromatic chemicals that could also be generated from lignin as a starting material. Examples include but are not limited to benzene derivatives, phenols, toluene, catechol, coniferyl & coumarate alcohols, p-coumaric acid, ferulic acid, syringaldehyde and sinapyl alcohol for example.

None of these compounds are currently manufactured from lignin, but a number of notable milestones have been met with regards to R&D in this area.

For example, Biorizon is an EU funded shared research center that is currently developing a novel technology for the depolymerization and fractionation of lignin. They aim to generate a range of 'bio-aromatic compounds' derived from the breakdown of lignin, and they are now in the process of scaling-up production with a view to produce lignin-based building blocks for the fine chemicals industry. A lignin depolymerization pilot plant, also known as the LignoValue pilot plant, is currently under construction in Flanders, and this facility aims to manufacture around 250 kg of functional bio-aromatics daily. It should be operational by mid-2022, and once plant construction has been completed, and the technology demonstrated at pilot scale, this system will correspond to a TRL of 6.^{86, 87} Biorizon aims to begin producing bio-aromatics on a commercial scale by 2025, therefore this could be an application area of considerable interest in the near future. The exact bio-aromatic compounds that are of interest to this project are not specified, presumably a result of the commercial sensitivity associated with the novel process under development.

A range of bio-aromatics can be obtained from lignin, including complex phenols such as vanillin, syringaldehyde, and ferulic acid, in addition to basic aromatics such as benzene, toluene and the three isomers of xylene (BTX) (Figure 5). BTX compounds are produced in very large volumes globally, and are important starting materials for the synthesis of a wide range of end-products (e.g. phenol, TNT, nylons, epoxy resins, polyesters, and polyurethanes for example) that can be used across a variety of different industry sectors.⁸⁸ BTX compounds account for roughly for 60% of all aromatics currently available on the marketplace, and due to their prevalence, there is an opportunity for lignin-derived alternatives to also enter the market.⁸⁹ However, at present the development lignin-based BTX aromatics are still very much in the R&D phase, and experts indicate that commercial scale production may not begin for another 10-20 years.

Figure 5: Benzene, toluene and xylene (BTX) compounds.



Key players involved in the development of lignin-derived BTX include:⁹⁰

- 🌱 FPIinnovations;
- 🌱 Alberta Pacific Forest Industries;
- 🌱 Fibria Innovations (Formally Lignol Energy Corporation);
- 🌱 Weyerhaeuser Company;
- 🌱 Lignoworks;
- 🌱 Anellotech Inc.;
- 🌱 Virent;
- 🌱 BioBTX;
- 🌱 Biochemtex;
- 🌱 VTT;
- 🌱 Bio Innovation Growth mega Cluster (BIG-Cluster);
- 🌱 Wageningen University.

As the synthesis of many compounds from lignin depends on depolymerization and fractionation reactions, it can therefore be assumed that lignin fractions that contain a higher degree of β -O-4 linkages are better suited to the production of fine and commodity chemicals. Low molecular weight and high purity lignins are also favorable. However, with regards to lignin solubility requirements, this will vary depending on the specific conditions of a given reaction, and since no routes to BTX have yet been commercially developed, it is unknown whether water soluble (i.e. lignosulfonates) or non-water soluble lignins (i.e. all other varieties) would be required for these applications.

An alternative method of producing chemicals from lignin is through the use of gasification, a technology that converts carbonaceous raw materials, such as coal, biomass, and lignin into a gaseous product called synthesis gas (syngas). Syngas consists primarily of carbon monoxide (CO) and hydrogen (H₂), and it can be used for the production of fuels (e.g. naphtha, petrol and diesel), for the generation of power, and for the synthesis of commodity chemicals (e.g. ethylene, methanol, acetic acid, formaldehyde, DME, DMSO, methyl acetate and polyolefins). Although gasification is not typically used to generate aromatic chemicals (which has been the focus of this section), this technology is worth mentioning as it shows potential for the production of a wider range of value-added chemicals from lignin. However, despite it being a commercially available technology when used for the treatment of fossil-derived fuels, gasification has not yet been developed for the processing of lignin, with research only carried out at lab/pilot scales thus far, representing a TRL of around 4-5.⁹¹ All types of lignins are believed to be compatible with gasification.

6.1.2 Oil Field Applications

Another interesting area of lignin application is in oil field operations, where lignin has been used by the industry since 1949, as a means of stabilizing emulsions in order to control water loss in lime-treated muds. Lignin prevents against the re-agglomeration of mud particles through steric and electrostatic repulsions i.e. decreasing the electrochemical attraction forces of clay, resulting in the decreased viscosity of drilling muds. This is known to decrease torque on drill stems, increases drilling rates and improves borehole conditions. Lignosulfonates are widely used in these applications due to their favorable water soluble properties and their effectiveness as a dispersant and surfactant. Furthermore, they are abundant, environmentally friendly, and cost effective materials. Given that lignin has been used for decades in oil field applications, products manufactured for these purposes have a TRL of 9.

6.1.3 Dye and Pigment Dispersions

Dyes and pigments are typically used in the form of aqueous dispersions. Therefore, the use of an effective dispersing agent is essential in order to prevent the agglomeration of particles and to increase the uniformity of suspended solids. This allows for dyes and pigments to be more easily applied to fibres.

Dispersants lower the interfacial tension between immiscible liquids and increase the repulsive forces between suspended particles to prevent them from settling. This improves the technical properties of multiphase systems such as rheology, lifetime, and function. Given that dyes and pigments are often used in aqueous environments, the dispersants used in these systems should therefore be water soluble, thus lignosulfonates are widely used. Furthermore, the high molecular weights of lignosulfonates are able to prevent the coagulation of particles due to their large size, and they are able to keep dispersions separated. These applications are therefore, not suited to lignins derived from biomass pretreatment prior to the production of cellulosic ethanol (unless they undergo prior modification to make them more hydrophilic). Given that lignin is widely used in dye and pigment dispersion applications, the associated TRL of developments in this area is assumed to be 9.

6.1.4 Battery Production

Another high-value application of lignin can be found in the production of batteries. Due to its highly aromatic nature, lignin can be used for the fabrication of low-cost, activated, and well-ordered carbons, whereby free electrons contained within the benzene rings of lignin can move between layers and subsequently conduct electricity (as is the case for fossil-derived graphite). This makes lignin suitable for a range of functions when used in battery manufacturing, including as:

- ✦ Expanders;
- ✦ Electrodes;
- ✦ Electrolytes;
- ✦ Dispersants; and
- ✦ Binders.

In lead-acid batteries, lignin can be used as a battery expander – a material that is added to the negative plates of these batteries to improve the performance and the life of the battery. There are number of

commercial examples of lignin-battery expander products that are currently on the market. These include: Vanisperse A and Maracell XC-2 by Borregaard LignoTech, and Vanillex by Nippon Paper Industries for example.

The greater the surface area of lead particles, the greater the discharge capacity of the battery. Organic expanders adsorb onto the surface of lead particles, and through Van der Waals forces of repulsion prevent small lead particles from becoming larger crystals. This leads to greater interaction with the electrolyte. This enables higher ion transfer between the negative and positive, both for discharge and re-charge.

Vanisperse A by Borregaard is the world's leading sustainable organic lead battery expander – it is considered the industry standard. However, all of the products highlighted above are also commercially available and are used by industry. They therefore correspond to a TRL of 9. These products are typically based upon the use of highly modified lignosulfonates, that are treated with alkalis at high temperatures so as to oxidate lignins to generate oxylicignins. During this process the lignosulfonates become partially desulfonated. The favored characteristics of these modified materials are:⁹²

- 🌿 Low average molecular weight lignin;
- 🌿 High carboxyl group content (i.e. highly oxidized);
- 🌿 Low methoxy group content;
- 🌿 Low organic S content.

Lignosulfonates are primarily used here, given the properties required by oxylicignins for their use as organic expanders, they are relatively reactive lignin compounds, which makes them suitable for modification. They are also water soluble, which means that they are well suited to the aqueous environment within lead acid batteries.

In addition to lead-acid batteries, lignin can also be used in lithium-ion batteries. When these batteries are charged, lithium ions in the cathode move to the anode, where they interact with carbon particles and are stored until the battery is used. At present, the main material used as the anode is often graphitic carbon which is typically derived from petroleum coke. However, by instead using lignin, batteries not only become more sustainable and partially renewable, but they are also able to demonstrate faster charging and perform better at low temperatures.

Stora Enso, one of the world leading manufacturers of kraft lignin is currently developing the use of dried lignin to create a bio-based, renewable alternative to graphite, that can be used for the production of anodes. At their newly constructed pilot facility at the Sunila Pulp Mill in Finland, Stora Enso are able to manufacture a hard carbon powder (a highly refined and solid form of carbon) which can then be used to produce electrode sheets and rolls. Finally, these hard carbon electrodes can be combined with positive electrodes, a separator, an electrolyte, and other components to produce a lithium-ion battery. Stora Enso currently markets the product of this process as "Lignode",⁹³ and this technology is currently developed at a pilot scale, and so it demonstrates a TRL of around 4-6. Stora Enso utilizes kraft lignin for the production of their Lignode, but research carried out by other industry players indicates that other lignin varieties can also be used for the production of electrodes, as it is the high carbon content of lignin that makes it compatible in these applications. Furthermore, low molecular weight and high purity lignins are also favored for these applications.

In terms of the use of lignin in for the production of batteries, electrode manufacturing appears to be one of the most widely investigated applications, and a patent review of the types of developments in this area highlighted that research is mainly focused in China. Presumably because it is the world's largest market for lead acid batteries at present.⁹⁴ Examples of companies conducting R&D in the area of lignin electrodes over the past decade include:

- ✦ Shanghai Hanhe Biological New Material Tech Co Ltd. (2021) (China);⁹⁵
- ✦ Kaiying Power Supply & Electrical Equip Co Ltd (2019) (China);⁹⁶
- ✦ Taizhou Lituo Energy Co Ltd (2019) (China);⁹⁷
- ✦ Changsheng Electrical Jiangsu Co Ltd. (2018) (China);⁹⁸
- ✦ Chaowei Power Co Ltd. (2016) (China);⁹⁹
- ✦ Eco Environmental Investments Company Limited (2015) (China).¹⁰⁰

6.1.5 Carbon Fibers

Carbon fibers are high-strength, light-weight materials, and their use within composite materials takes advantage of their strength, stiffness, low weight, lack of corrosion and heat insulation. They are most commonly manufactured using polyacrylonitrile (PAN), and primarily used in the following applications:

- ✦ Construction;
- ✦ Electronics;
- ✦ Transportation;
- ✦ Aviation.

One of the key drivers in promoting the carbon fiber market is the potential for the light weighting of automobiles. However, their high cost (~\$35/kg) can often inhibit their use in many commercial applications.

Lignin-based carbon fibers on the other hand with their low associated costs and their sustainable nature, can offer a promising alternative. Furthermore, lignin has been reported to also offer additional benefits to carbon fibers, such as the elimination of toxic substances involved during preparation, lower melting temperature and faster stabilization compared to PAN and pitch-based alternatives.

In order to obtain lignin-based carbon fibers, lignin is first spun into fibers by extruding filaments from a melt or solvent swollen gel. Then these fibers are thermally stabilized in air where the lignin fiber is oxidized, and then fibers pyrolyzed under nitrogen or in an inert atmosphere in order to carbonize the polymer chains and eliminate the presence of volatile hydrocarbons, oxidized derivatives, carbon gases, and moisture.¹⁰¹

Historically, the first lignin-based carbon fiber was developed in 1969 by Nippon Kayaku Co. and their patent described a process that used alkaline lignin and liginosulphonates, and spun by melt, wet and dry extrusions. The company started commercializing these fibers in 1968 for gasket applications and developed a pilot plant in 1970. Their lignin carbon fiber material was given the name 'Kayocarbon fiber'. However, Nippon ceased production of these fibers because of the poor mechanical properties demonstrated by the fiber.

However, despite this ceasing of lignin carbon fiber production by Nippon, development has continued in this area and is demonstrated by the publication of various patents by key industry players over the past two decades:

- 🌱 Lignol (2011),¹⁰²
- 🌱 Fraunhofer (2011),¹⁰³
- 🌱 Stora Enso (2014),¹⁰⁴
- 🌱 Unitika Ltd (2014),¹⁰⁵
- 🌱 Lignin Industries (formally Ren Com AB) (2020),¹⁰⁶

The first ever lignin carbon fiber, produced by Nippon, originated from the use of kraft lignin however various other lignin types have been investigated as a raw material for this application.¹⁰⁷ This demonstrates that carbon fiber production is relatively flexible in terms of the types of lignins that can be used. However, the main problem in the development of lignin carbon fibers to date is that none have been able to achieve the mechanical properties that match the general performance of carbon fibers produced from conventional starting materials. This appears to be the main barrier to commercialization at present. Thus, the TRL for lignin carbon fiber production remains around 4 to 6.

Given that lignin-based carbon fibers cannot generally compete with PAN-based carbon fibers in terms of their mechanical properties, they are believed to be best suited to applications that do not require exceptional strength, such as automotive interiors for lighter weight cars and fiberglass production (as opposed to uses in the aerospace industry for example). Therefore, there could still remain a considerable opportunity in carbon fiber applications for lignin in the future.

6.1.6 Hydrogels

Hydrogels are three-dimensional (3D) networks of polymers; their hydrophilic structures make them capable of absorbing and holding large amounts of water within their 3D networks. Hydrogels have gained significant attention in biomedical sectors as they can be used for drug delivery, tissue engineering, and antimicrobial materials.

Recently, lignin has been viewed as a promising material for the production of hydrogels, because of its high antioxidant and antibacterial properties. It also has a high absorption capacity, which makes it suitable for potentially removing undesirable metabolites from wounds. Furthermore, due to lignin's high mechanical strength, its use in hydrogels helps protect wounds from further injury or contamination.

There are several ways that lignin can be combined with other materials to construct composite wound dressings. For example, lignosulfonates can be used to construct crosslinked polyvinyl alcohol (PVA) with lignin to form a hydrogel, and when a solution of silver nitrate is also added the resulting hydrogel is able to demonstrate enhanced antimicrobial properties as well as good elasticity.¹⁰⁸ However, as with many other applications, lignin typically requires a considerable amount of modification in order for it to be used effectively as a medical material.

As their name suggests, hydrogels are used in aqueous environments and so any lignins used in these applications must also be water soluble. Thus lignosulfonates are largely used here. Research however,

appears to be largely dominated by academia, with limited industrial support for hydrogel applications at present. It is therefore assumed that the TRL of hydrogel development is approximately around TRL 4, thus commercialization in this area is highly unlikely any time soon.

6.2 Mid-Value Market Applications of Lignin

Mid-value applications of lignin typically represent the largest segment of lignin's total market – believed to cumulatively correspond to around 60% of lignin consumption by volume. Lignin products classified as “mid-value” would typically expect to command a market price of between \$300-750 per ton.¹⁰⁹ The most commercially interesting of these applications are discussed below.

6.2.1 Concrete Additives

Lignin as a concrete additive is one of the most prominent uses of this material on the market currently. It is widely used within admixtures as a dispersant agent/surfactant. Concrete is typically made up of three major components: Portland cement, water and aggregate. However, chemical admixtures often form a vital fourth ingredient. These admixtures are used to modify the properties of concrete (or mortar, or grout) so that they are more suited to their intended applications. Admixtures generally contain organic compounds, or mixtures of organic and inorganic compounds.¹¹⁰

In cement-water dispersions, the ‘tail’ end of the surfactant gets adsorbed onto cement particles. Fine particles of cement in water, which under normal circumstances would floc together due to physical and chemical forces of attraction between them, are now dispersed as a result. This causes deflocculation and leads to a greater surface area of cement particles being exposed to water, and a more even finish upon drying. Modified lignosulfonates are highly suited to these applications as they exhibit high molecular weights (i.e. they are ideal for keeping concrete particles apart) and they are water soluble. These applications are therefore, not suited to lignins derived from biomass pretreatment prior to the production of cellulosic ethanol (unless they undergo prior modification to make them more hydrophilic). Lignin is widely used in concrete applications at present, and so the associated TRL is believed to be 9.

6.2.2 Fertilizers

Fertilizers are common agrochemicals that have been developed on a commercial scale using lignin as a starting material. There are a number of different lignin products currently available on the market for this function, indicating that this application corresponds to a TRL of 9.

A specific example of where lignin has been developed for use in the agrochemicals industry is for the production of slow-release fertilizers. The high adhesive strength of lignin ensures that fertilizer grains feature effective binding and are resistant to abrasion, as well as the effective release of components when exposed to weather conditions. The latter point is achieved due to the excellent water solubility of lignin. Thus, lignosulfonates are typically used in these applications.¹¹¹

6.2.3 Phenol Formaldehyde Resins

Phenolic resins are synthetic thermosetting resins. Due to the highly polyaromatic nature of lignin, it has been studied extensively as a monomer for the production of phenolic resins. This is driven by a desire to replace fossil-derived phenols with renewable, biobased components. Phenol formaldehyde (PF) is the most common and most widely used of these phenolic resins on the market, and at present it is widely used as an adhesive, as a binder, as a coating, and as a laminate material.

Lignin can be used in the synthesis of phenol formaldehyde to form a highly cross-linked aromatic resins with partial biobased content. There has been a considerable amount of research in this area but to date, only limited quantities of phenols have been replaced by lignin, due to the low reactivity typically associated with these substitute materials.¹¹² Nevertheless, phenol formaldehyde resin production continues to be a key research area when looking to identify new commercial applications of lignin. Recent developments have focused largely on their use as adhesives, particularly for the manufacture of structural wood products such as plywood, oriented strand board and fiberboard. Over the past decade, a number of notable companies have filed patents on the production of lignin phenol formaldehyde resins for use in adhesive applications, demonstrating that this remains a key area of interest amongst industry. They include:

- 🌱 Stora Enso (Finland) (2021);¹¹³
- 🌱 FPInnovations (Canada) (2012, 2018 & 2020);¹¹⁴
- 🌱 Jining Mingsheng New Material Co., Ltd. (China) (2018);¹¹⁵
- 🌱 Compagnie Industrielle De La Matière Végétale (CIMV) (France) (2018);¹¹⁶
- 🌱 Trespa International (Netherlands) (2018);¹¹⁷
- 🌱 Georgia Pacific (US) (2015 & 2016);¹¹⁸
- 🌱 Lignol Innovations (Canada) (2010 & 2011);¹¹⁹
- 🌱 Weyerhaeuser Company (US) (2013).¹²⁰

Developments in this area typically focus on utilizing low molecular weight and highly modified lignins to enhance their reactivity prior to the production of adhesive resins. If unmodified lignin is used in applications that require fast curing, such as thermoset resin production (e.g. phenol formaldehyde), then the resulting manufacturing process is likely to be highly inefficient and therefore expensive.¹²¹ The most popular methods of modifying lignin include: methylation, phenolation, demethylation, and reduction. Methylation and phenolation are considered the most commercially interesting on account of their relatively low process costs. Lignin that contains a higher degree of aliphatic hydroxyls and phenolic hydroxyls are believed to be more reactive starting materials and thus, better suited to these processes. The use of the pre-methylated lignin in the presence of synthetic phenol formaldehyde in particular, is considered to be one of the most significant advances towards the development of commercial lignin-based adhesives,¹²² and this has led to a number of lignin phenol formaldehyde adhesive products entering the market. Key examples include:

- 🌱 Riga ECOlogical – developed by Latvijas Finieris is a lignin-based wood adhesive that is employed for the production of plywood products in place of traditional PF-based glues. This product was developed in partnership with Stora Enso and uses their Lineo™ kraft lignin as the principal source of biobased phenols.^{123, 124}

- 🌱 BioBond – developed by UPM’s WISA Plywood business is also a kraft lignin-derived wood glue used for the production of plywood.¹²⁵
- 🌱 Bloom – developed by Arpa Industriale in partnership with Wageningen University is a new lignin-based adhesive used in Arpa HPL and FENIX NTM® product lines i.e. for the production of high quality interior panels.¹²⁶

Although produced in relatively small quantities at present, these examples highlight that lignin-based phenol formaldehyde adhesives have already achieved market commercialization and thus, and thus processes are considered to have a TRL of 9. They also demonstrate that kraft lignin is the main lignin variety to be used here, a fairly unreactive material that has undergone modifications in order to make it suitable. Thus similar lignins derived from alkali pretreatment for example, in addition to other biomass pretreatment processes could also be suitable for the production of phenol formaldehyde resins.

In addition to the commercial use of lignin phenol formaldehydes as wood adhesives, there is also potential for them to be used in the production of foams, as well as in flame retardant system,¹²⁷ but this application is still believed to be in a relatively early stage of research.

6.2.4 Acrylonitrile Butadiene Styrene

Lignin has also been investigated as an additive to ABS (acrylonitrile butadiene styrene), a polymer widely used to manufacture high strength materials. Lignin has been reported to provide increased stiffness and reduced cost. However, lignin is generally incompatible with ABS polymers, forming large domains of lignin with poor interfacial adhesion with the ABS matrix. Therefore, there has been a considerable amount of research around the development of lignin compatible ABS polymers.

Furthermore, since lignin is a natural product, its incorporation in plastics like ABS adds renewable content and reduces the environmental impact of these materials. Notable developments in this area include those from:

- 🌱 Prisma Renewable Composites; and
- 🌱 Lignin Industries AB

Prisma Renewable Composites have developed and licensed technologies for making ABS and other high-value composites and polymers from lignin. They claim that their lignin-based ABS plastic replacement (trademarked as BioLAN™) costs less, has a higher tensile strength, a higher UV resistance, and lower VOC levels than standard ABS resins. They have partnered with industrial partner, Yanfeng Automotive Interiors (YFAI), a supplier of high-quality automotive interior solutions to develop a range of car part interiors.¹²⁸ Another key development in this area is by Lignin Industries AB who have developed RENOL a lignin-based polymer that can be used alongside thermoplastics such as ABS, PE, PP and biobased PLA as a functional additive. In an extruder, lignin and bio components are mixed into RENOL granulates that are designed for plastic manufacturing processes and used in the same way as fossil counterparts. RENOL can be blended with most existing thermoplastics, and three application areas are currently being targeted: films; infill for artificial football pitches; and injection-molded products.

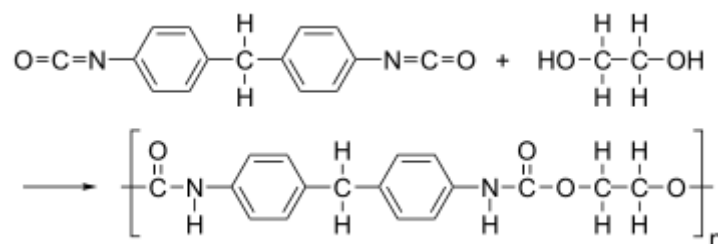
In terms of the types of lignins required for the technologies outlined above, a range of lignins are potentially suited. For example, kraft lignin, is the main type of lignin to be used for the production of Prisma’s ABS composites at present. However, it does require prior modification in order to enhance the properties of the end polymer. This process is flexible with regards to the types of lignins that can be used here, demonstrating that any lignin produced via biomass pretreatment could be used for this application downstream.

The technologies discussed in this section have not yet made it to market. But it is believed that they have been developed to around TRL 4 to 6. Given the increasing trends towards the development of more sustainable plastic products, this application offers a huge amount of potential in terms of future growth. Key limitations here will likely be the high cost of production.

6.2.5 Polyurethanes

Polyurethanes (PUs) are commonplace polymers composed of monomers linked together by urethanes, traditionally formed by reacting di- or tri-isocyanates with polyols (Figure 6). They are some of the most versatile polymers currently available commercially and exhibit exceptional mechanical properties. As such, they are widely used in the insulation of fridges/freezers, building insulation/construction, cushioning for furniture, mattresses, car parts, coatings, adhesives, rollers and tire, composite wood panels, shoe soles, and sportswear for example.

Figure 6: An example of polyurethane production.



Polyurethanes can be tailored to be either rigid or flexible, with properties depending on: the types monomers used; the degree of cross-linking; and the synthesis procedure employed. Generally, soft elastic polymers can be generated from flexible long chains and limited cross-linking. Shorter chains with a higher cross-link density typically leads to rigid and tough products. Research indicates that lignin can be incorporated into polyurethane structures either by: the direct use of lignin as a macromonomer; as a fractionated lignin; or as modified lignin.¹²⁹ Furthermore, as is the case for conventional polyurethanes, lignin polyurethanes can also be used in a range of functional applications i.e. to produce ridged foams, films, and adhesive coatings for example.¹³⁰

The presence of many hydroxyl groups enables lignin to be used as polyols. There has been a considerable amount of research in this area, but no developments have yet become a commercial reality. For example, the following companies have all filed patents that outline methods for developing lignin-polyurethane systems within the past two decades:

- 🌱 Rampf Holdings GMBH (2019);¹³¹
- 🌱 Tianjin Jiameite Bicycle Co Ltd. (2020);¹³²

- 🌱 Hexion Inc (2019);¹³³
- 🌱 Huntsman (2019);¹³⁴
- 🌱 Jinan Jiaotai Information Technology Co Ltd. (2015);¹³⁵
- 🌱 Enerlab 2000 Inc (2016);¹³⁶
- 🌱 China Petroleum & Chemical Corporation (2021);¹³⁷
- 🌱 Synpo (2014).¹³⁸

Much like the other polymer applications discussed in this report thus far, polyurethanes are not manufactured in aqueous environments, and so lignosulfonates are not compatible with these applications. Therefore, kraft lignins are primarily investigated in this area, and lignins derived from different pretreatment processes are believed to also be suited here. Given that these developments have not yet made it to any considerable scale, it can be assumed that the TRL of these technologies has reached a maximum of 4-6.

6.2.6 Rubber Reinforcements

Lignin has the potential to be used as a reinforcing filler in place of the carbon black currently used by the rubber industry. Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as fluid catalytic cracker (FCC) tar, coal tar, or ethylene cracking. The utilization of alternative fillers within the rubber industry has therefore gained considerable attention due to the increasing environmental concerns over the toxic effects of carbon black on human health and the natural environment. As such, lignin is considered a cheap, abundant and renewable alternative to carbon black, and although it is not currently used commercially, there is the potential for this material to enter to the market in the future.

Lignin has several favorable characteristics such as good mechanical and physico-chemical strength, biodegradability, antioxidant properties, and excellent thermal stability. However, the incorporation of lignin into a rubber matrix is not straightforward due to the high polarity of lignin molecules which contributes to strong self-interactions.¹³⁹ Therefore chemical modifications are required in order to improve the dispersion of lignin, or a compatibilizer is required in order to enhance the interfacial adhesion between the lignin and the rubber matrix.

Research indicates that either kraft lignins or lignosulfonates could be used in these applications. Demonstrating that any type of lignin could be used here, provided that it undergoes sufficient modification to make it compatible with rubber. Smaller molecular weight lignins are however, favored in these applications. As no significant commercial progress has been made with this application of lignin, production processes can be assumed to have a TRL of around 4.

6.2.7 Food Additive

Due to the favorable surface-active (i.e. surfactant) properties of lignin, this material has therefore been investigated as a food additive for the preparation of emulsions (mixtures of water and oil) and foams. Furthermore, it is believed to reduce the degree of oxidation that takes place in food products. Given the areas where lignin is used here (i.e. emulsions), the water solubility of lignin is essential.

Lignin has been investigated for its use in the manufacturing of baked goods, and it has found to result in fluffy textures making it a potentially suitable substitute to the use of whole eggs and egg yolks. Furthermore, it has been found to function as an emulsion in mayonnaise. However, at present these applications do not appear to have been used at any significant scale, suggesting that they have only been developed at lab-scales thus far. Indicating a TRL of around 4.

6.3 Low-Value Market Applications of Lignin

Low-value bulk applications represent a sizeable segment of lignin's total market – believed to cumulatively correspond to around 30% of lignin consumption by volume. Lignin products classified as “low-value” would typically expect to command a market price of less than \$300 per ton.¹⁴⁰ The most commercially interesting of these applications are discussed below.

6.3.1 Dust Control

Lignin shows an affinity for binding with other polar and non-polar compounds. Small dust compounds are absorbed by lignosulfonate and form a larger, heavier complex which settles the dust. It can be also used for dust control in ceramic manufacturing, synthetic fertilizer production and delivery, in cement clinker milling, and in concrete mixing.¹⁴¹ Lignosulfonates are primarily used for these applications given that water soluble properties are required. It is applied as an aqueous spray, and once applied to the surface in question, water evaporates from the lignosulfonates and dust particles are trapped.

Lignosulfonates have a long history of use on roads, as a method for dust control and surface stabilization. Dust movement can thus be controlled by spraying a road surface with an emulsion of asphalt, lignin and water – this has been found to be more effective than traditional chlorides (e.g. magnesium chloride) on gravel roads that contain higher levels of sand. Lignin is well suited for a variety of uses such as parking lots, driveways, and road shoulders, where pavement is too costly and dust conditions can become unmanageable. Furthermore, lignosulfonates can be used on unpaved roads to reduce environmental issues from airborne dust particles. Given that this is a widely used application of lignin, production processes have a TRL of 9.

6.3.2 Heat Pellets

Heat pellet production is another key area where lignins are used at present. These are widely used as alternatives to firewood, due to their ease of storage and high energy density.

Lignin-based heat pellets may consist primarily of lignin, or they may be incorporated as a binder in conventional wood pellets. Either kraft lignin or lignosulfonates can be used here. The structure of wood pellets can sometimes be fragile and disintegrate to generate fines (i.e. crushed or powdered material) during handling and transport without the addition of additives. Therefore, lignin can be added as a binder to improve pellet strength. The use of lignin within pellet production can also reduce the friction in pelleting equipment resulting in increased production rates and lower costs. Less friction also leads to the requirement for less equipment maintenance, and so lignin is an ideal additive when used in the production of pellets.¹⁴²

The lower degree of fines generated by pellets containing lignin as a binder are believed to be a result of the increased densification of the pellet matrix, with higher lignin contents shown to result in pellets with better bonding characteristics between particles. During the pressing process, high temperatures cause lignin to reach its glass transition temperature (i.e. it changes from a rigid, solid polymer to a soft, melted material) allowing it to act as a form of cement within the pellet.¹⁴³

Lignin-based pellets demonstrate high calorific values and high bulk densities, and such products are already available on the market, demonstrating a TRL of 9. For example, Danish energy company, Verdo, produces “black pellets” made from lignin and wood fiber.¹⁴⁴

6.3.3 Animal Feed

Similarly to heat pellets, lignin can also be used in the production of animal feed pellets, with lignosulfonates largely used here. The water soluble nature of these materials means that they are able to act as prebiotics for the gut health of animals, as well as pellet binders. Furthermore, the addition of lignosulfonate leads to higher moisture retention within the pellets, improved gelatinization of starches at low temperatures, improved amino acid digestion, reduced degradation of vitamins, and it is easy to use for the optimization of different diet formulations.¹⁴⁵ Lignin binders for animal feeds are readily available on the market, which demonstrates a TRL of 9. The key players in this market include, amongst others:

- 🌿 Sappi;
- 🌿 Comet Bio;
- 🌿 Borregaard;
- 🌿 Green Agrochem.

Other types of lignins could also be used in animal feed applications due to the binding properties that lignins generally exhibit. But the non-water soluble nature of lignins other than lignosulfonates would result in no dietary benefits added to the pellet feed i.e. they would pass straight through the dietary system of the animal.

6.3.4 Asphalt Binder

Asphalt is typically made of 95% mineral aggregates and 5% binder, and more than 1 trillion metric tonnes is produced every year. One way to reduce the carbon footprint of asphalt is to use a renewable material as the binder. Lignin has been used for this in several tests e.g. Stora Enso’s Lineo™ lignin has already been used in several projects in Central Europe, with kraft lignin used as the raw material for production.

The water stability of an asphalt mixture can be improved by adding around 0.3% of lignin fibers. Hydrophobic lignins are favorable here as they prevent the breakdown of asphalt when it comes into contact with water. Asphalt-emulsifying agents containing softwood sodium lignin salts with an average molecular weight of 200–100,000 have been reported to exhibit suitable hydrophilic–lipophilic balance (HLB) values and frothing ability, slow demulsification speeds, and strong foam stability.¹⁴⁶

Although lignin is not currently used as a major ingredient in asphalt as of yet, the world's first "bio-road" was constructed by infrastructure company Roelofs, which suggests that this application technology has reached a TRL of around 6 and demonstrates that there is commercial interest in this area.

6.3.5 Lignin-Oil

In addition to the combustion of lignin, it can be converted into an oil for use as a source of energy. The company RenFuel has invented a technology that transforms lignin into a lignin oil called LIGNOL. This oil originates from lignin in black liquors (i.e. derived from the kraft process) and, following conventional refining it can be mixed with regular diesel and gasoline as a drop-in fuel to reduce the need for fossil fuels in the short term. LIGNOL is also believed to be well suited to being blended with kerosene, aviation fuel.

Using a patented catalytic process, RenFuel are able to convert lignin into renewable lignin oil in an environmentally friendly and energy efficient process. Currently kraft lignin is used for this process, but other lignins could also be used here.

RenFuel are currently developing the production of LIGNOL at a pilot scale, with tests now in the final phase and reported to be showing positive results. The project has also began developing drawing, process descriptions and cost estimates for a commercial LIGNOL plant in the near future.¹⁴⁷ This therefore, suggests that this technology has been developed to TRL 4-6, and there is promise for timely developments to be made in this area going forward.

6.4 Summary of Lignin Applications

To summarise the work presented in this section, there are wide range of possible applications available to lignin and the most commercially interesting have been discussed. Table 3 outlines the key features of lignin that are generally required by each application. In general, it can be said that where lignin is used as a dispersant, surfactant or emulsifier, lignosulfonates are typically used, as these applications rely on water soluble properties. Furthermore, in applications where high reactivities are required, lignosulfonates are also commonly used as they tend to exhibit a higher number of reactive bonds (e.g. vanillin production and other fine/commodity chemical manufacturing).

Where water solubility is not necessarily required by a given application, there is an opportunity for kraft lignin (and indeed other types of pretreatment derived lignins) to be used. Lithium ion batteries, heat pellets and lignin oil, which depend on lignin for its high carbonaceous content and calorific value are notable examples. The production of polymers is another key area where kraft lignin maybe employed as a replacement for fossil derived aromatics in a polymer's chain (e.g. phenol formaldehyde, ABS, polyurethanes, and carbon fibers). Furthermore, polymers are often manufactured in organic environments, therefore lignosulfonates are not suitable here as they are only soluble in aqueous systems. Finally, in applications where hydrophobicity is specifically required, kraft lignins are typically selected as the lignins of choice, and this also presents an opportunity for other types of pretreatment derived lignins to be used (a good example here is the use of lignin in the production of asphalt).

Table 3: Summary of lignin applications and the typical properties required by each one.

Value	Application	Lignin Properties			
		Molecular Weight	High Purity?	Solubility	Key Features
High	Vanillin	Low	Yes	Water	High reactivity
	Oil Field Applications	High	No	Water	Highly polar
	Dye Dispersion	High	Yes	Water	Highly polar
	Lead Acid Batteries	Low	Yes	Water	Highly oxidated
	Lithium Ion Batteries	Low	Yes	Organic	High carbon content
	Carbon Fibers	Low	Yes	Organic	High reactivity
	Hydrogels	High	Yes	Water	Highly polar
Medium	Concrete Additive	High	No	Water	Highly polar
	Fertilisers	High	Yes	Water	Highly polar
	Phenol Formaldehyde	Low	Yes	Organic	High reactivity
	ABS	Low	Yes	Organic	High reactivity
	Polyurethanes	Low	Yes	Organic	High reactivity
	Rubber Reinforcement	Low	Yes	Organic	High reactivity
	Food Additive	High	Yes	Water	Highly polar
Low	Dust Control	High	No	Water	Highly polar
	Heat Pellet	Variable	No	Variable	High carbon content
	Animal Feed	High	Yes	Water	High reactivity
	Asphalt Binder	Variable	No	Non-water	Hydrophobic
	Lignin Oil	Variable	No	Organic	High carbon content

7 Lignin Market Opportunities

Having reviewed the key applications currently available to different types of lignins, the following section outlines the most promising market opportunities. Target markets for each application are outlined, and the size of the total addressable market indicated, including a geographical breakdown where possible.

Overall, it is estimated that around 100 million tonnes of lignin are currently generated around the globe.¹⁴⁸ But of this total, only 2% is believed to be extracted and used in commercial applications. The remainder is typically combusted at the site where it is used for the generation of heat and power. This demonstrates that the actual volume of lignin currently used by the global market is in the region of 2 million tons. The total value of this market was estimated to be in the region of \$970 million in 2020,¹⁴⁹ indicating that that average price of lignin in this market approximately \$485 per ton.

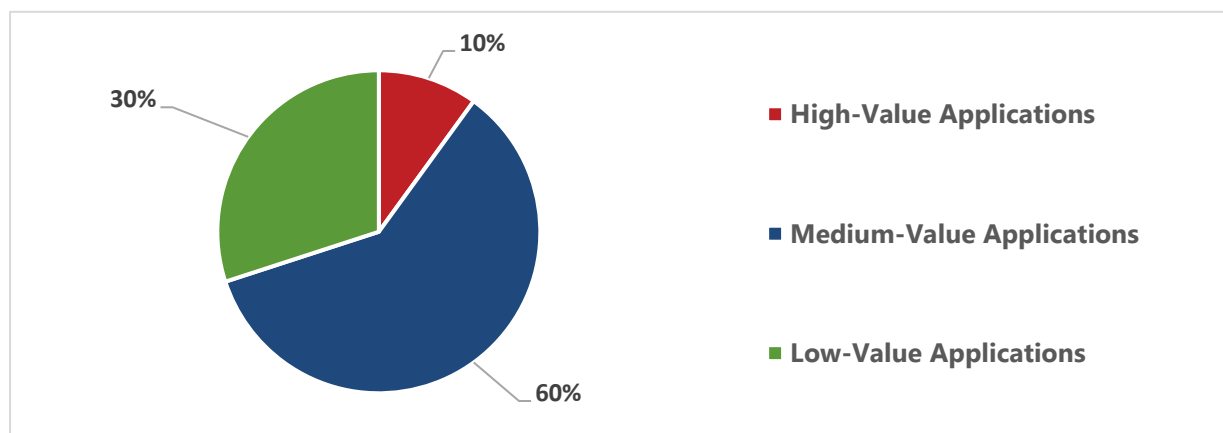
Lignosulfonates currently account for roughly 90% of all commercial lignin produced annually, corresponding to a worldwide production volume of approximately 1.8 million tons.¹⁵⁰ The world's leading manufacturer of this type of lignin is Borregaard LignoTech, based out of Norway. They are believed to produce approximately 40% of all the lignosulfonates manufactured around the globe.

Other key players operating within the lignin market include:

- ✦ MeadWestvaco Corporation;
- ✦ Tembec Inc., Domtar Corporation;
- ✦ Domsjö Fabriker AB;
- ✦ Changzhou Shanfeng Chemical Industry Co. Ltd.;
- ✦ Nippon Paper Industries Co. Ltd.;
- ✦ UPM-Kymmene Corporation;
- ✦ Asian Lignin Manufacturing Pvt. Ltd.;
- ✦ Lignol Energy Corporation; and
- ✦ Green Value.

The lignin market is typically split into high, medium and low-value applications, which corresponds to lignin prices of: greater than \$750 per ton; between \$300-750 per ton; and less than \$300 per ton respectively. It is estimated that high-value applications account for roughly 10% of the current lignin market, while medium-value applications account for 60%, and low-value applications account for 30% of the market. Within each of these market segments either kraft lignins or lignosulfonates are typically used, depending on the specific application.

Figure 7: Market share of lignin applications by value.



However, as has been demonstrated throughout this report, there is also the potential for pretreatment derived lignins to also be used in the applications reviewed. When looking to identify the most promising market opportunities associated with alternative lignin varieties, it is useful to consider:

- 1) The **suitability** of different lignins with the applications considered
- 2) The **technology readiness** of these potential uses of lignin; and
- 3) The **value** associated with each lignin application (i.e. high, medium, or low-value application).

The compatibility of different pretreatment derived lignins with the applications addressed in this report has been analysed. A qualitative description of the findings are highlighted Table 4. Lignins that are understood to be highly suited to a given application are highlighted in green. Those that are believed to be less compatible but still show potential for use in a given application without the need for modification are highlighted in yellow. Those that are deemed incompatible with a given application

but where suitability could be improved if lignin modification is carried out are highlighted in orange. Finally, where lignins are not believed to be compatible with a given application and where properties are not thought to be improved through the use of modification, they are highlighted in red.^{iv}

Table 4: Lignin applications and their suitability to different pretreatment processes.

Value	Application	TRL	Pretreatment Process					
			Alkali	Dil. Acid	Conc. Acid	Liquid Hot Water	Organosolv	Steam Explosion
High	Vanillin	9	*	**	**	**	*	*
	Oil Field Applications	9	*	**	*	*	*	*
	Dye Dispersion	9	*	**	*	*	*	*
	Lead Acid Batteries	9	**	**	**	**	**	**
	Lithium Ion Batteries	4-6	****	***	***	****	***	****
	Carbon Fibers	4-6	**	***	****	****	**	**
	Hydrogels	4	*	**	*	*	*	*
Medium	Concrete Additive	9	*	**	*	*	*	*
	Fertilisers	9	*	**	*	*	*	*
	Phenol Formaldehyde	9	**	***	****	****	**	**
	ABS	4-6	**	***	****	****	**	**
	Polyurethanes	4-6	**	***	****	****	**	**
	Rubber Reinforcement	4	**	***	****	****	**	**
	Food Additive	4	*	**	*	*	*	*
	Dust Control	9	*	**	*	*	*	*
Low	Heat Pellet	9	****	****	****	****	****	****
	Animal Feed	9	***	**	**	***	**	***
	Asphalt Binder	6	****	****	****	****	****	****
	Lignin Oil	4-6	****	****	****	****	****	****

- * = **unsuitable**
- ** = **potentially suitable but modification is required**
- *** = **potentially suitable and modification not deemed necessary**
- **** = **highly suited**

Upon closer inspection, the table above indicates that dilute acid pretreatments are the most flexible processes in terms of the applications in which resultant lignins can be used. However, where sulfuric acid is employed, there is the possibility that subsequent lignins will contain a small amount of sulfur containing compounds, which are generally associated with unpleasant odors. Therefore, when used in downstream applications (i.e. resin/composite production), end products may emit a characteristic smell. In general however, in order to verify the true potential of these materials in certain applications,

^{iv}) The results illustrated in this table, are assumptions made following the desk-based research presented in this report. It gives an indication of the compatibility of different lignin varieties with certain applications, but this can only be truly verified via lab-based research. Thus, application testing should be carried out to verify the results presented in Table 4.

dilute acid lignins must undergo application testing and possible modifications in order to be deemed suitable in practice.

When taking into consideration lignin applications that are already commercially developed (i.e. TRL 9), it is clear that the most promising opportunity for pretreatment derived lignins lies in the production of biomass pellets for heat applications. This can be considered an immediate opportunity as all lignin varieties are believed to be compatible here and they can be incorporated into pellets with relative ease.

The production of phenol formaldehyde resins, presents another promising near-term opportunity, and one that is of higher value than heat pellets. This application is believed to be suited to acid pretreated and liquid hot water pretreated lignins, without the need for modification. However, in order to demonstrate that this is the case, products will need to be developed and application testing carried out. Thus, for this reason, phenol formaldehyde resins are not an immediate term opportunity but one which shows potential for the near future.

The remaining applications highlighted in Table 4 that show a TRL of 5 or above, can be considered longer-term opportunities. These demonstrate potential due to the fact that either:

- ✎ applications are believed to be suited to the use of pretreatment derived lignins, but where these markets have not yet been commercially developed for lignin; or
- ✎ the market has been commercially developed for the use of kraft/acid sulfite lignins, but where the use of other types of lignin would likely require some form of modification in order to be suitable.

7.1 Near-Term Market Opportunities

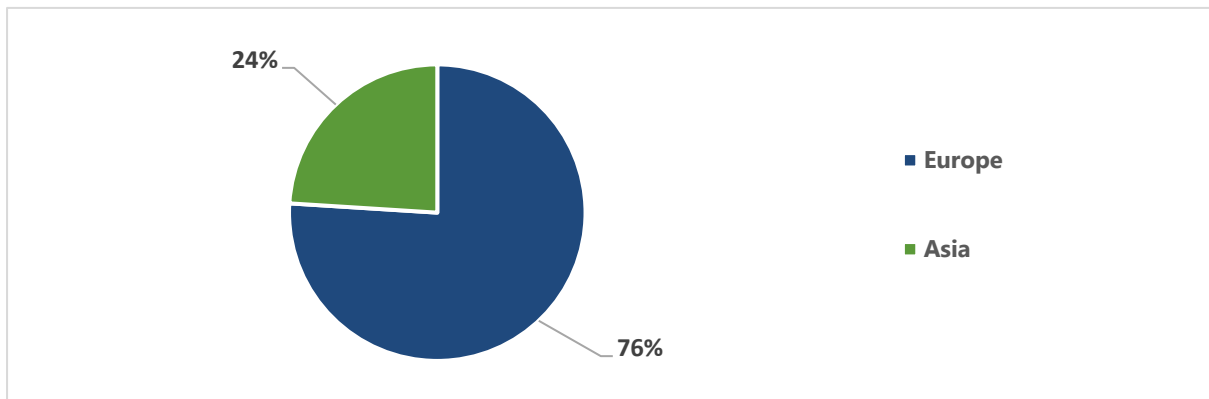
The markets for the most promising near-term opportunities are outlined in the following section.

7.1.1 Heat Pellets

Heat and fuel pellets are the only application which demonstrate immediate market potential for use of pretreatment derived lignins.

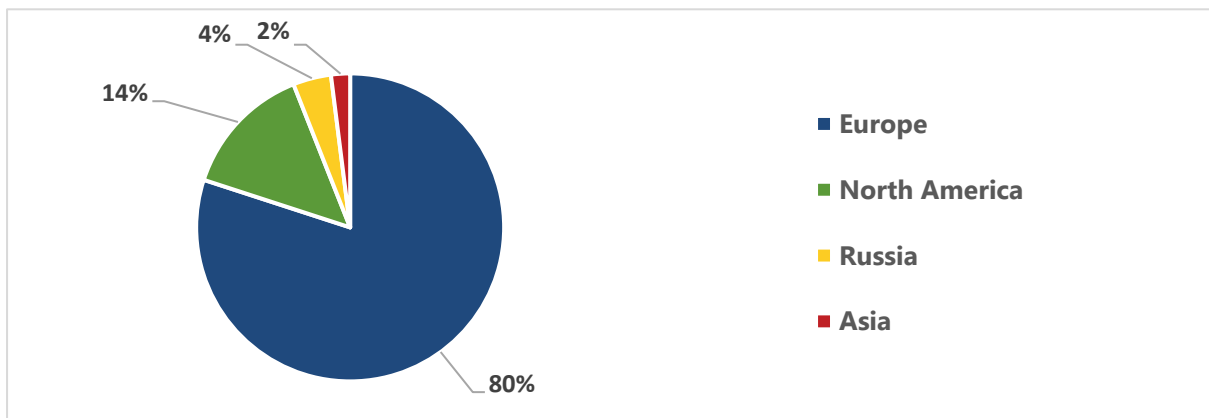
In 2019, it was estimated that the total global demand for wood pellets was roughly 37 million tons, with an annual growth rate of around 6%. It is understood that approximately 19 million tons of pellets are used by industry around the world (i.e. for the generation of power, CHP, and large district heating) and around 18 million tons of pellets are used for the generation of heat in residential and commercial boilers. Of the demand for pellets in industry, around three quarters currently comes from Europe, while one quarter comes from Asia (Figure 8).¹⁵¹

Figure 8: Global industrial demand for wood pellets in 2019.¹⁵²



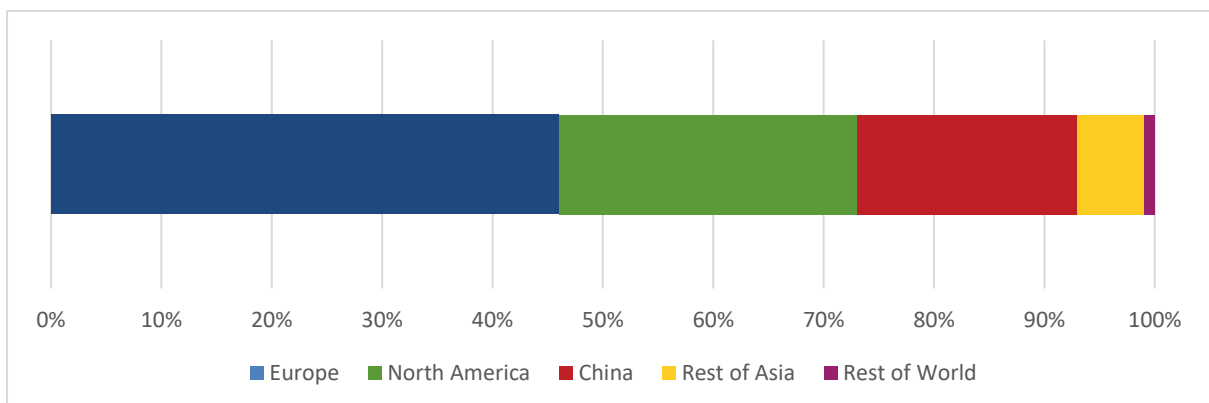
Of the demand for pellets in residential and commercial boilers, around 80% originates from Europe and only 2% comes from Asia (Figure 9). However, Asia has shown considerable growth in recent years, particularly in Thailand, Indonesia, Vietnam, Malaysia and China.

Figure 9: Global heating demand for wood pellets in commercial and residential boilers (2019).¹⁵³



In terms of pellet production, Europe dominates, followed by North America and China. In Indonesia, it was estimated that approximately 100,000 tons of wood pellets were manufactured in 2016.¹⁵⁴

Figure 10: Global wood pellet production.¹⁵⁵



Key players involved in the global heat and fuel pellet market include:

- ✦ Enviva;
- ✦ Graanul Invest;
- ✦ Drax;
- ✦ Fram Renewable Fuels;
- ✦ Segezha Group;
- ✦ Lignetics;
- ✦ Biopower Sustainable Energy Corp.;
- ✦ Asia Biomass;
- ✦ Verdo.

Given that the global pellet market is anticipated to increase considerably over the next few years, the valorisation of lignin for heat and fuel applications offers a considerable opportunity going forward.

7.1.2 Phenol Formaldehyde Resin Market

Phenol Formaldehyde resins represent another promising short term market opportunity for pretreatment derived lignins. This application is already developed to a TRL of 9, and it is believed that alternative lignins could be used. However they will need to undergo product development and application testing to demonstrate that they are suitable for these applications.

It is estimated that roughly 6 million tons of phenol formaldehyde resins are produced annually around the world, corresponding to a global market value of around \$11 billion, and an average phenolic resin price of approximately \$2000 per ton (i.e. \$2 per kg).¹⁵⁶

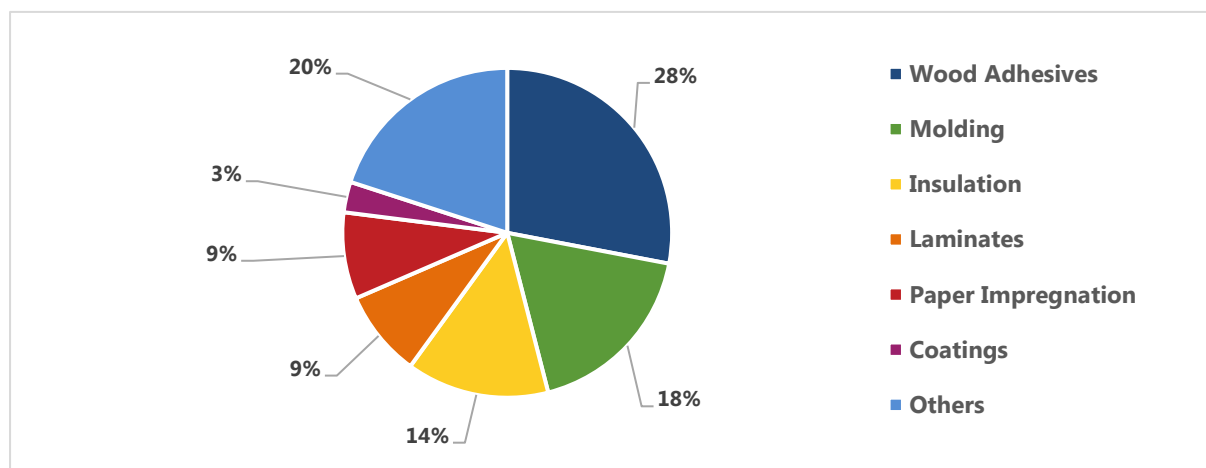
This market is split into two, novolac and resole resin types – novolacs are resins that are relatively unreactive and need a cross-linking agent for them to fully polymerize; resoles however, are reactive resins and are self-curing due to the presence of reactive side groups. Lignin is primarily used to substitute phenols in the latter type of resin and it is believed that these resoles account for roughly 50% of the entire phenol formaldehyde market¹⁵⁷ (i.e. an estimated 3 million tons).

The major global producers of phenolic resins include:

- ✦ Arizona Chemicals (Sylvares Copolymers);
- ✦ Ashland (Aroclene);
- ✦ GP Chemicals (GP and Leaf resins);
- ✦ Hexion (Bakelite), Mitsui Chemicals (MiLex);
- ✦ Quantum Composites (ESC Phenolic).

With regards to the applications that phenol formaldehydes are used in, the most prominent is their use as wood adhesives as shown in Figure 11, followed by molding, insulation, laminates, paper impregnation and coatings.

Figure 11: Key applications of phenol formaldehyde resins.¹⁵⁸



In terms of geography, the Asia Pacific (APAC) region dominates this market presently, due to high rates of growth within the building and construction industries. APAC is also expected to remain the key player in the phenol formaldehyde market over the next 5 years due to a high demand for resins and laminated products in the region.¹⁵⁹

Lignin is primarily used as a substitute for phenol in phenol formaldehyde resins, various studies have investigated the replacement of phenol with varying amounts of lignin. A conservative estimate expects that around 50% of phenol can be replaced by lignin in these resins.¹⁶⁰

The overall phenol formaldehyde market currently accounts for around 6 million tons of resin, but it is recognized that the commercial opportunity for lignin lies within the resole segment of the market, which represents roughly 3 million tons. The typical mole ratio of formaldehyde to phenol in conventional resins ranges from around 1.2-1.9 moles of formaldehyde per mole of phenol.¹⁶¹ This means that for the 3 million tons of resole resins currently available on the market, around 2 million tons is phenol. If lignin is able to then replace around 50% of phenols within this resin mixture, this equates to a total target market of around 1 million tons of lignin required.

However, it is not realistic to assume that lignin will be able to capture 100% of this target market, and so a reasonable assumption is that a 10% capture rate would be a better estimate. This indicates that the market potential for lignin in phenol formaldehyde markets is around 100,000 tons.

7.2 Longer-Term Market Opportunities

Longer-term market opportunities include those that are believed to be suited to the use of pretreatment derived lignins, but where these markets have not yet been commercially developed (i.e. they are less than TRL 9). Longer-term applications also include those where the market has been commercially developed for the use of kraft/acid sulfite lignins, but where the use of other types of lignin would likely require some form of modification and thus, process development in order for them to be suitable. The most interesting of these longer-term opportunities will be discussed in the following section to give an indication as to the size of these potential markets.

7.2.1 Carbon Fiber Market

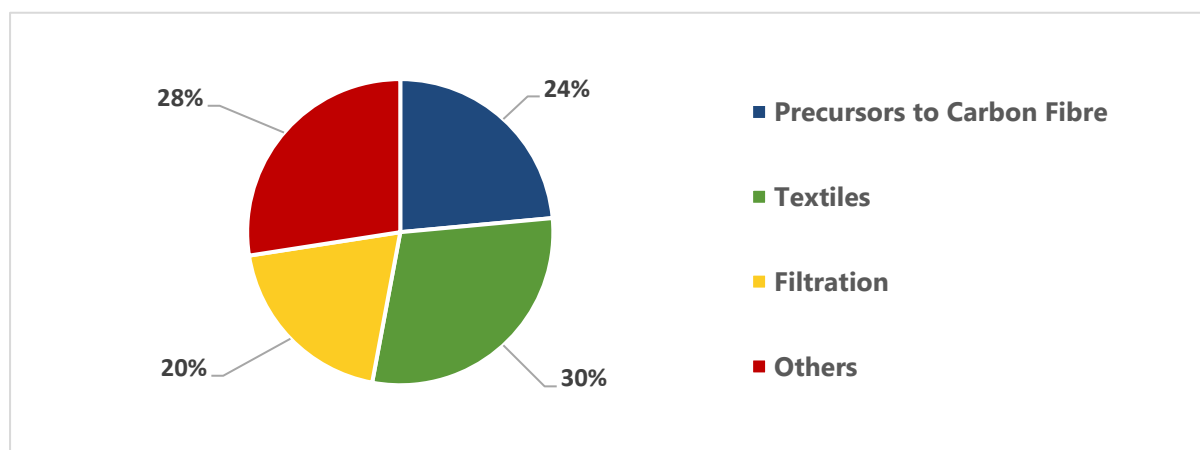
Carbon fibers have been identified as an interesting opportunity for pretreatment derived lignins due to the fact that they are a high value application, and could be used without the need for significant modification. This technology however, is currently at a TRL 4-5. Hence why it is considered to have longer term potential.

Carbon fibers contain at least 90% carbon by weight. They are light, flexible, and very strong materials. Various types of carbon fiber are manufactured across the globe, but the most common varieties are based on the use of polyacrylonitrile (PAN) which accounts for more than 80% of the global carbon fiber market. Due to the highly aromatic nature of lignin, it has the potential to replace PAN in carbon fiber applications, which currently has an estimated market value of around \$8 billion.^v The size of the global PAN market in terms of production volume is currently estimated to be around 2.5 million tons.^{162, 163} However, this market is showing little evidence of growth at present.

Dralon are currently the market leaders in PAN fiber production, they produce just short of 200,000 tonnes of PAN annually and represent around 8% of the global market. It is thought that PAN production is focused in China which represents around 40% of the market. The APAC region has been the market leader for a number of years, due to substantial demand in the textiles sector. In North America, demand for PAN is driven by high tech applications e.g. in military and commercial aircrafts.

It is believed that around one quarter of the PAN market is currently used in the production of carbon fibers. This is the application that has been identified as an opportunity for lignin going forward, and represents a total market size of 625,000 tons.

Figure 12: Market share of applications in the polyacrylonitrile market.¹⁶⁴



However, lignin based carbon fibers do not have the high mechanical strength properties of PAN fibers and therefore, are limited to applications where high strength is not necessarily required (e.g. automotive interiors to lightweight vehicles, and to replace fiberglass in composites). Unlike applications in aerospace engineering for example. The automotive market has been identified as the best

^v) Although PAN itself is not an aromatic polymer, it becomes so following oxidization and stabilization.

opportunity for lignin market integration as it generally requires low modulus materials (e.g. 172 GPa) with low tensile strength (e.g. 1.72 GPa) properties which lignin based fibers could provide.¹⁶⁵

7.2.2 Lithium Ion Battery Market

Lithium ion batteries have also been identified as an interesting long-term opportunity for pretreatment derived lignins due to the fact that they represent a high value application, and show potential suitability to be used without the need for significant modification. This technology however, is currently developed to around TRL 5-6, and thus more development needs to take place in order for it to become a commercial reality.

In 2016, the lithium ion battery market resulted in the production of around 28 GWh of electricity. Whereas today, it can supply upwards of 400 GWh, representing a battery market value of around \$40 billion. This highlights considerable growth within this market over the last 5 years, with this trend set to continue over the next decade. The imminent increase expected in the production of electric vehicles (EVs), as well as a surge in demand for additional grid storage, is anticipated to drive this market going forward.¹⁶⁶ By 2025, it is expected that around 1,500 GWh will be generated by lithium ion batteries.¹⁶⁷ Key players in the production of lithium ion batteries across the globe include:

- 🌿 Tesla;
- 🌿 BYD Company;
- 🌿 A123 Systems;
- 🌿 Panasonic;
- 🌿 Samsung SDI;
- 🌿 Toshiba;
- 🌿 LG Chem;
- 🌿 Saft;
- 🌿 Sony;
- 🌿 Contemporary Amperex Technology.

Figure 13: Lithium ion battery market share by application (2019).¹⁶⁸

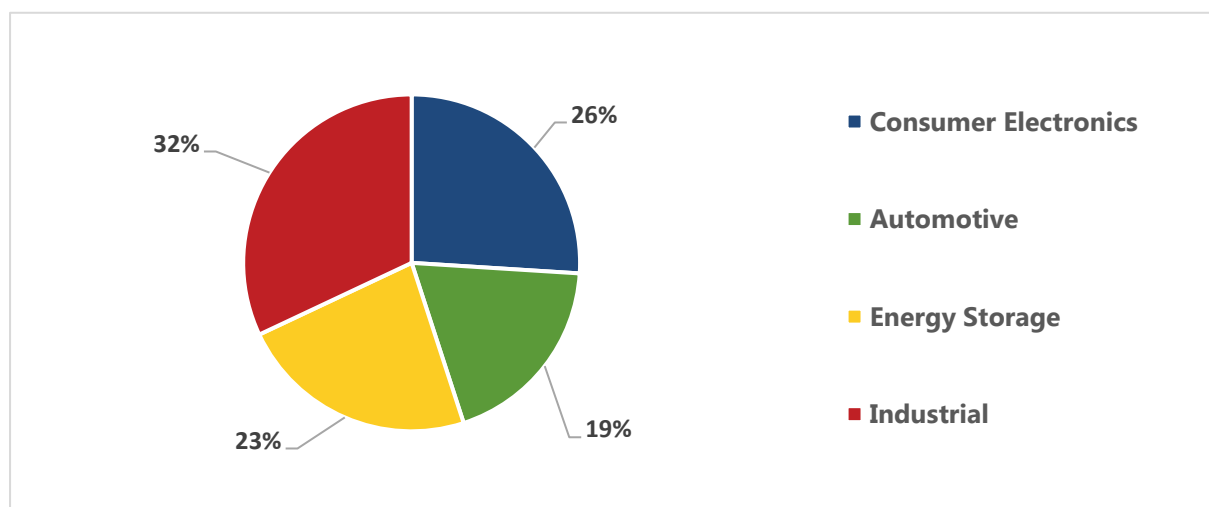


Figure 13 outlines how the lithium ion battery market is split in terms of application, with around one quarter used in each of the consumer electronics and energy storage sectors, around one fifth in automotive applications, and a third used industrially.¹⁶⁹ This spread of market applications is expected to change considerably as EVs become more prominent in the near future.

In terms of geographical factors, China currently dominates the world's lithium-ion manufacturing market, producing almost 80% of all lithium ion batteries at present. While China is expected to remain the leading country in the production of these batteries, Europe is poised to significantly increase its production capacity. By 2025, Europe is expected to account for around 25% of the global capacity.¹⁷⁰

With regards to lignin use within this market, it has primarily been investigated for the production of anodes. At present, the anodes of lithium ion batteries are largely made out of graphite. The type of graphite used is called spherical graphite (SPG), and is manufactured from flake graphite (produced from graphite mines) which is 'rounded' and upgraded to 99.95% purity. The process used for the production of SPG is expensive and often results in the waste of up to 70% of graphite flakes. The resulting material costs up to \$3,000 per ton when uncoated (over three times the price of graphite flakes), and can sell for between \$4,000-12,000 per ton when coated (depending on the end market sector). In comparison, lignin has the potential to be a much more cost effective material used here.¹⁷¹

To give an indication as to how much graphite is used by this industry, in just one hybrid electric vehicle, around 10 kg is used, while up to 70kg can be used in a fully electric vehicle.¹⁷² To put this into context, around the world, there are believed to be around 2.4 million hybrid electric vehicles on the road and 4.8 million battery electric vehicles. This corresponds to a total amount of graphite used in these vehicles of 24,000 tons and 48,000 tons respectively. Between the years of 2018 and 2019, approximately 600,000 new hybrid electric vehicles entered the market, while 1.5 million new battery electric vehicles were sold, equating to 111,000 tons of graphite required that year for the production of electric cars.¹⁷³ This is anticipated to rise considerably over the next few years, with the market expected to experience a compound annual growth rate (CAGR) of between 12-20%.^{174, 175} Therefore, lignin has the potential to satisfy a portion of this demand in the future.

7.2.3 Lead Acid Battery Market

Lead acid batteries are a high-value commercially available application of lignin. However, in order for pretreatment derived lignins to be used in this market, they will need to undergo modification to become better suited. They therefore, have the potential to become an interesting market opportunity in the future.

The global lead-acid battery market is expected to grow by a CAGR of around 4% over the period of 2020-2025, with factors such as a growing automotive sector and the low cost of lead expected to drive this market. However, factors such as the declining price of lithium-ion batteries and the growth in electric vehicle sales is anticipated to restrain the growth of lead-acid battery market in the coming years.¹⁷⁶ The current value of the global lead acid battery market is around \$50 billion.¹⁷⁷

7.2.4 Vanillin Market

Vanillin is another high-value application of lignin that is currently developed for the use of lignosulfonates to TRL 9. However, in order for pretreatment derived lignins to be used in existing synthesis methods, they will need to undergo modification. Or, novel routes for the production of vanillin will need to be developed. Therefore, it is an interesting market opportunity that could potentially prevail in the longer-term. However, as a specialty chemical the size of market opportunity is limited.

Vanillin is a high-value market compound that is used primarily as a flavor, a fragrance and a pharmaceutical ingredient. The value of this market is believed to be around \$400 million,¹⁷⁸ and associated demand is in the region of around 20,000 tons per year.¹⁷⁹ At present, the current vanillin market is dominated by petroleum-based vanillin, which demonstrates a market value of around \$10 per kg. Vanillin synthesized from lignin on the other hand is believed to cost in the region of \$100-200 per kg i.e. roughly 10-20% more expensive than prominent synthetic vanillin varieties. Vanillin synthesized from lignin is therefore able to capture around 15% of the current vanillin market at present (i.e. around 300 tons), and further growth in this area will be influenced by costs associated with lignin compared with crude oil.

7.2.5 Acrylonitrile Butadiene Styrene (ABS) Market

ABS is another interesting polymer that could be produced using pretreatment derived lignins. This technology however, is currently developed to around TRL 5-6, and thus more development needs to take place in order for it to become a commercial reality. Nevertheless, it is an interesting application that shows potential in the long-term.

It is estimated that around 11 million tons of acrylonitrile butadiene styrene (ABS) is currently produced annually around the world, corresponding to a global market value of around \$27 billion, and an average polymer price of around \$2500 per ton (i.e. \$2.5 per kg).^{180, 181}

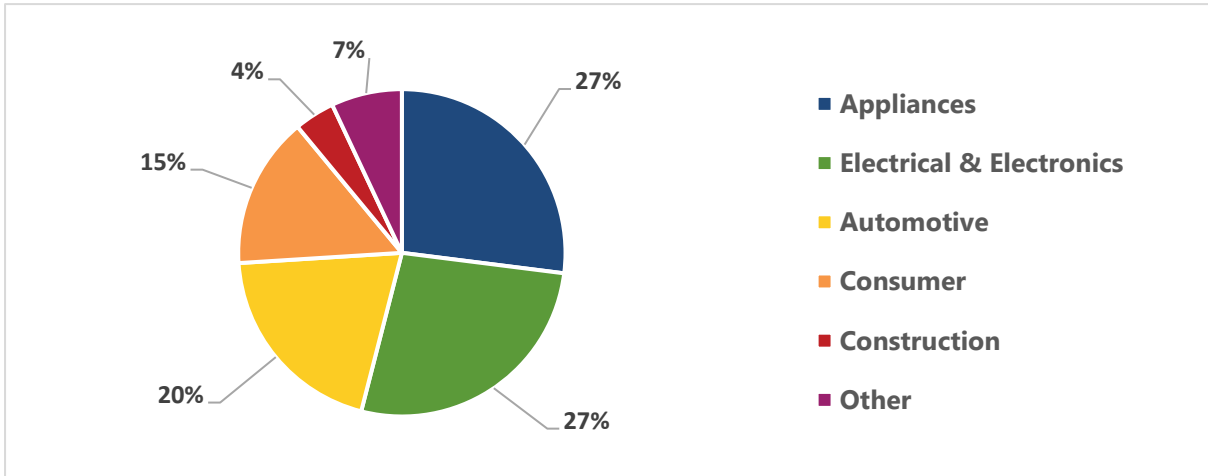
ABS is primarily used for the production of appliance parts, electrical and electronic products, automotive components, and consumer goods (as highlighted in Figure 14). Given that a key area identified for the use of lignin has been in automotive applications, this corresponds to a market size of around 2.2 million tons of ABS, and accounts for approximately 12.5% of all automotive plastics used in the production of passenger cars e.g.in bumpers, seating, dashboards, interior trims, center consoles, and light fittings.¹⁸²

Key players within this sector include:

- 🌱 LG Chemicals;
- 🌱 Chi Mei Corporation;
- 🌱 Formosa Plastics;
- 🌱 KKPC;
- 🌱 SABIC;
- 🌱 Styron;

- 🌿 BASF SE;
- 🌿 DuPont;
- 🌿 INEOS Styrolution;
- 🌿 Trinseo;
- 🌿 Toray; and
- 🌿 Mitsui Chemicals.

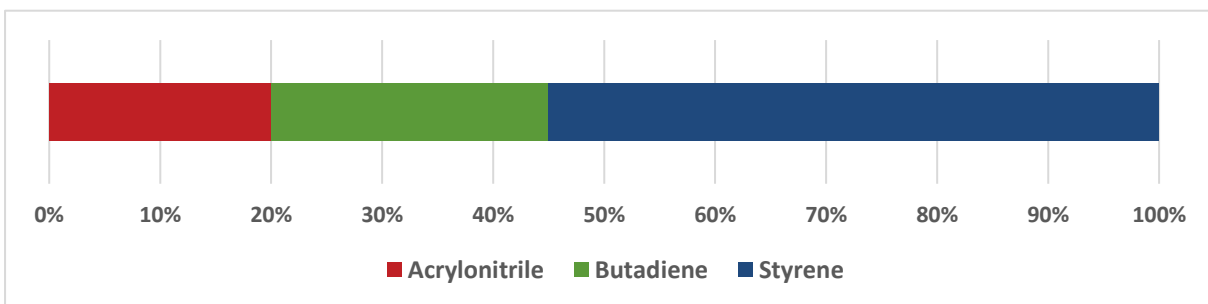
Figure 14: Key applications of acrylonitrile butadiene styrene.^{183, 184}



The demand of ABS is driven largely by the APAC region due to significant growth occurring across the automotive and construction industries in this region. Furthermore, a rise in demand for electronic & electrical products manufactured in China, India, Taiwan, and Japan, is also expected over the next decade. North America is the second largest consumer of ABS worldwide, followed by Europe, a result of the high presence of automotive component, and a demand for high-performance and lighter weight car parts in this region.

ABS is made up of three polymers: acrylonitrile, butadiene and styrene, which can be used in varying ratios, to create resin products with variable properties. However, in general, ABS is composed in the proportions as shown in Figure 15.¹⁸⁵

Figure 15: Typical composition of ABS resins.¹⁸⁶



Due to the highly aromatic nature of lignin, it can be used to replace fossil-derived styrene in ABS, this accounts for roughly 55% of the components within ABS (on a molar basis). Based on this, it can be estimated that of the 11 million tons of ABS generated annually around the globe, roughly 6 million

tons of this is made up of styrene. This therefore, demonstrates the scale of possible opportunity available to lignin within this market.

However, at present, lignin is primarily being developed for use in the automotive sector, which accounts for a market of around 2.2 million tonnes. This equates to a volume of around 1.3 million tonnes of styrene used in this market segment. If lignin is used to replace just 30% of styrene within ABS products in the automotive sector, then this means that around 400,000 tons of lignin would be required. If just 10% of this targetable market could be captured following the commercialization of lignin-ABS resins over the next few decades, then this would correspond to an approximate lignin demand of around 40,000 tonnes.

7.2.6 Polyurethane Market

Polyurethanes could also represent a longer term market opportunity. This is considered a mid-value market and currently stands at a TRL of between 4 and 5. Pretreatment derived lignins may or may not need to undergo modification in order to be used in these applications.

In general, the current global market volume of polyurethanes is 24 million tons¹⁸⁷ and correspond to a market value of around \$60 billion.^{188, 189} This indicates an average resin price in the region of \$2,500 per ton (i.e. \$2.5 per kg). Key drivers of this market are believed to be in the use of polyurethanes in building and construction and in the production of memory foams.¹⁹⁰ However, competition from fiberglass and polystyrene foam is expected to hinder growth in this market. The APAC region dominated the global market share of polyurethane consumption. With growing construction activities and rapid urbanization in China and India, the use of polyurethanes are increasing in this region.¹⁹¹

7.2.7 Asphalt Binder Market

Asphalt binders have been identified as another potential long-term opportunity for pretreatment derived lignins. However, this represents a low-value application and it has not been developed commercially with any type of lignin as of yet (i.e. TRL6). This means that considerable development still needs to be made in this area.

It is estimated that around 120 million tons of asphalt are currently produced around the world,¹⁹² corresponding to a global market value of around \$2 billion, and an average asphalt price of around \$16 per ton. In recent years, the APAC region has overtaken North America as the largest regional market for asphalt, driven primarily by activity in China and India. However, it is expected that growth in China will slow as the country shifts its focus to repairing and maintaining current roadways rather than expanding its road network.

Lignin has been identified as a potentially suitable binder for the production of asphalt. At present, around 15% of an asphalt product consists of binder material, corresponding to an overall volume of approximately 18 million tons. Asphalt binders function as inexpensive, waterproof, thermoplastic adhesives – i.e. the glue that holds roads together. The most common type of binder currently used by the asphalt market are derived from petroleum refining, to achieve the necessary properties for paving purposes the binder must be produced from a carefully chosen crude oil blend, and processed to an

appropriate grade. Occasionally additives (usually polymers) are blended, or reacted with binders to enhance their properties.¹⁹³

It is estimated that existing binders typically cost as little as \$0.02/kg as a by-product of petroleum refining. Therefore, lignin would need to compete with the economics of using this inexpensive material if it is to be used at any significant scale as a binder in the future. However, given the sheer size of the asphalt market and the readily available nature of existing binders at a low price, it is highly unlikely that lignin will play any major role in the production of “bio-roads” in the near future

7.2.8 Lignin oil

Finally, lignin oil is also recognized as a possible long-term opportunity. Pretreatment derived lignins are deemed compatible with this application. However, this represents a low-value application and it has not been developed commercially with any type of lignin as of yet.

LIGNOL has the potential to replace both gasoline and diesel as a drop in fuel. However, given the commercial availability of other biofuels in the market (i.e. biodiesel and bioethanol), this novel lignin fuel would be expected to compete with these types of materials. Furthermore, given the way that the transport sector is heading (i.e. towards electric vehicles) there is potentially less of an opportunity here than perhaps was expected.

7.3 Market Summary

To summarise the key markets for pretreatment derived lignins, the most promising near-term opportunities lie in the production of heat pellets and in the production of phenol formaldehyde resins. In these applications, pretreatment lignins are believed to be compatible, and the markets for these applications are understood to be developed (i.e. TRL 9) with conventional lignin products (i.e. kraft lignins and lignosulfonates).

However, a number of other market areas are also believed to demonstrate longer-term potential. In these cases, applications may have been deemed suited to the use of pretreatment derived lignins, but the markets for these applications may not yet have been commercially developed for lignin. Or, alternatively the market for a given application may have been commercially developed for the use of kraft/acid sulfite lignins, but with other types of lignins, modification is likely to be required for them to be deemed suitable for use. Such developments take time, and although opportunities have been identified here, their potential is not likely to be commercially realised at any point in the near future. Thus, they have been outlined as long-term opportunities.

8 Summary

At present, the majority of lignin generated around the globe originates from either an acid sulfite or a kraft pulping process. However, in regard to cellulosic ethanol production, neither the kraft nor the acid sulfite pulping processes are compatible pretreatment techniques, due to the substantial costs associated with the generation of quality cellulose for pulp and paper manufacturing. Alternative pretreatment technologies include: alkali, dilute acid, concentrated acid, liquid hot water, steam

explosion, AFEX, and organosolv processes. All of these technologies, with the exception of concentrated acid, AFEX and organosolv, are currently commercially available for the pretreatment of lignocellulosic biomass.

In terms of lignin recovery, steam explosion, organosolv, and alkaline pretreatments demonstrate the highest attainable yields. Followed by concentrated acid, dilute acid, and liquid hot water pretreatments. These pretreatment technologies also generate a wide range of molecular weight lignins. Those that produce high molecular weight lignins include dilute acid, concentrated acid and AFEX pretreatments, whereas alkaline, liquid hot water, steam explosion and organosolv pretreatments produce low molecular weight lignins. In general, all lignin fractions display a high number of phenol and hydroxyl groups. The presence of β -O-4 linkages and other labile bonds tends to correspond with the degree of lignin depolymerization i.e. smaller lignin fragments generally contain less of these reactive sites as they have been more extensively degraded. High molecular weight lignins are therefore, typically more reactive than low molecular weight compounds.

With regards to biomass compatibility, in general all pretreatment technologies are suitable for processing agricultural residues. Therefore, when considering the types of feedstocks that are readily available in Indonesia (e.g. rice/maize straw, oil palm empty fruit bunches, sugarcane residues and bagasse), all technologies could potentially be used as a means of pretreating biomass prior to cellulosic ethanol production. In terms of wood processing, hardwood is compatible with all pretreatment processes apart from AFEX, and softwood is believed to be processed most effectively using liquid hot water pretreatments.

In general, it can be said that all pretreatment technologies yield relatively impure lignins, with the exception of organosolv. Furthermore, no commercial pretreatment technologies are able to generate water soluble lignins (comparable to lignosulfonates).^{vi, 194} This is significant, as it means that no lignins obtained by these commercial processes are suitable for applications that require water solubility, unless of course additional modification processes are carried out (as has been demonstrated for kraft lignins).

The review of market opportunities for pretreatment lignins showed two options for technical development: 1) to take advantage of established markets for lignosulfonates through the sulfonation of suitable pretreatment lignins; and 2) new applications currently under development based on kraft lignin.

In addition to water solubility, many lignosulfonate applications rely on the relatively high molecular weights of lignosulfonates for their performance. Dispersant applications such as surfactants and emulsifiers require high molecular weight lignosulfonates to prevent the coagulation of particles, and therefore keep dispersions separated. With the possible exception of dilute acid lignins, lignin produced in pretreatment processes is of low molecular weight and therefore not suited to these applications.

Of applications currently under development using kraft lignin, polymer manufacturing (e.g. phenol formaldehydes, ABS, polyurethanes), composite manufacturing (either as binders/adhesives or through carbon fiber production) or for use in lithium ion battery production, offer interesting opportunities. In certain applications such as the production of phenol formaldehyde resin, the presence of residual sulfur

^{vi)} The BALI process developed by Borregaard however, is an interesting precommercial technology in this regard.

in kraft lignins can cause issue of malodors in end products resulting in the need for lignin desulfurization prior to use. The use of pretreatment lignin, free from sulfur, could offer process advantages and improved economics in these applications.

Other opportunities through the development of novel synthesis routes for the production of specialty and commodity chemicals may be interesting in the long term but have significant technical and economic hurdles to overcome. Some technical opportunities e.g. lignin as an asphalt binder or the production of lignin oil, are low value applications and the economic attractiveness of these markets would require more investigation.

However, with regards to the true extent of lignin suitability in any given application, the only effective way of verifying compatibility is to carry out application testing. Lignin is a highly complex molecule and there are a range of competing factors that can result in it being a suitable raw material.

In terms of key markets identified for pretreatment derived lignins, the most promising near-term opportunities lie in the production of heat pellets and in the production of phenol formaldehyde resins. In both these applications, pretreatment lignins are believed to be technically suitable, and can benefit from commercially developed processes (i.e. TRL 9) based on the use of conventional lignin raw materials (i.e. kraft lignins and lignosulfonates).

In addition to these near-term opportunities, there are a number of other applications that demonstrate market potential in the longer-term. In these cases, applications may have been deemed compatible with pretreatment derived lignins, but their markets may not yet have been commercially developed. Or, alternatively, the market for a given application may have been commercially developed for use with kraft/acid sulfite lignins, but in order to use other types of lignins, modifications may be required. The development of novel products and/or markets can take time, and although a number of opportunities have been identified here, their potential is not likely to be commercially realised at any point in the near future.

9 Conclusion

To conclude, there are several biomass pretreatment options that could be employed in the production of cellulosic ethanol. The most prominent examples have been reviewed, all of which result in the generation of lignin in varying yields and with slightly different properties.

On review of the properties of lignin derived from these pretreatment technologies several promising market opportunities have become apparent.

With regards to the compatibility of pretreatment derived lignins with different applications, dilute acid pretreatment appears to be the most flexible process in terms of the number of applications in which resultant lignins could be used. However, where sulfuric acid is employed, there is the possibility that subsequent lignins may contain a small amount of sulfur containing compounds, which are generally associated with unpleasant odors. Therefore, when used in downstream applications (i.e. resin/composite production), end products could emit a characteristic smell. Therefore for these applications non-sulfur based pretreatment processes may be favored for lignin production.

In terms of interesting market opportunities, there are a number of factors that have been considered, including:

- 1) The TRL of the application in question (i.e. is there an existing market to sell into?);
- 2) The suitability of the lignin for the given application (i.e. do the properties of lignin match up with those required for the application?);
- 3) The value of the application (i.e. is the chosen application/market likely to yield good economic returns?).

Based on these key factors, a key near term market opportunity has been identified in the production of biomass pellets for heat applications. This is already an application that has been developed commercially for lignosulfonate/kraft lignin use. The properties of lignins derived from pretreatments appears to be compatible with this application. However, this is a low-value application and thus, it may be more profitable to target an end-use that may yield better returns.

The conversion of pretreatment lignins into water soluble lignosulfonates may be possible depending on the target application and other technical requirements such as molecular size or distribution.

Another interesting near term application is in the production of phenol formaldehyde resins. The phenolic properties of lignin make it an ideal candidate to replace phenol. This application has been extensively developed using kraft lignin and is considered technically ready for commercialization.

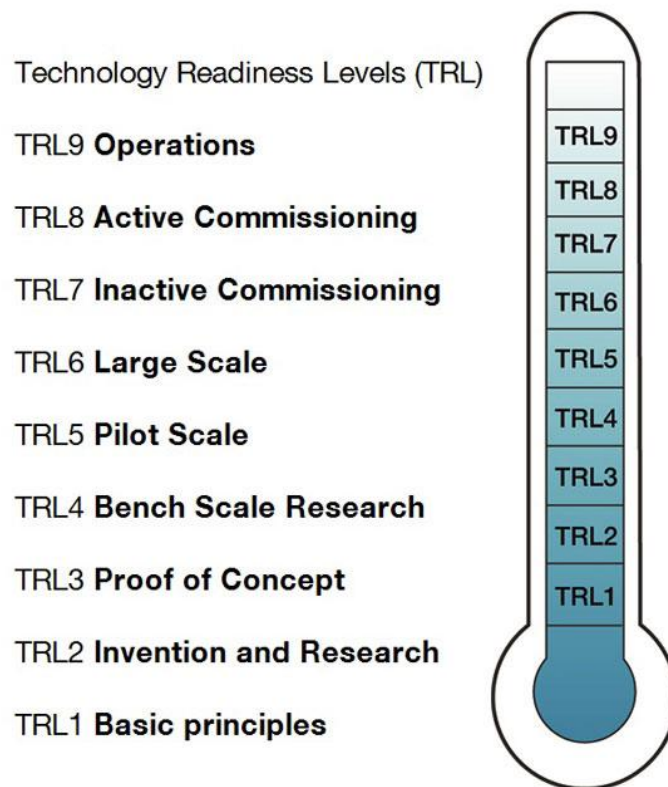
Although less developed than phenol formaldehyde resins, the production of carbon fiber for use in composites is considered an attractive target for development. Although technical restrictions may prohibit their use in high performance applications such as in aerospace, there may be an opportunity to incorporate these materials into automobiles as part of industry efforts on light weighting vehicles.

However, in all of these applications it is important to be aware that any novel lignins entering the market will not only compete with fossil-based alternative materials, but also with the conventional lignins that currently dominate the lignin market (i.e. kraft lignins and lignosulfonates). Therefore, any commercial project targeting specific lignin applications will require a detailed techno-economic and market analysis to determine the true extent of the opportunity.

Annex I – Technology Readiness Levels (TRLs)

Technology readiness levels (TRLs) are a means of reviewing at what stage a novel technology is operating at. It ranges from TRL 1 (basic principles are observed and reported) to TRL 9 (system proven in operational environment) (Figure 16).

Figure 16: Defining early technology readiness levels.¹⁹⁵



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