

ADDENDUM WHITEPAPER

BAFTA: BIO-AROMATICS FEEDSTOCK AND TECHNOLOGY ASSESSMENT

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Chapter 1: Lignocellulose as carbon feedstock

Fossil resources are one of the keystones of our global society. The exploitation of natural gas, coal and oil meets our needs for energy, materials and chemicals. This use cannot be sustained in the long term due to various reasons. Despite the frequent discovery of new reserves, our current use exceeds its natural replacement. This poses geopolitical issues and associated price fluctuations. However, it does not pose a supply problem in the short term as such, even if one considers the projected increasing demand for energy and chemicals. The biggest short-term problem is the linear model of the fossil-based economy. The associated emissions of greenhouse gases and toxic products cause environmental, climate and health problems.

Instigated by the increasing awareness of these negative effects, our society is gradually transitioning towards a more sustainable exploitation of its resources. Technologies for energy production are invented or rediscovered, using renewable sources such as wind, solar, hydro, bio and geothermal energy. However, the production of synthetic materials and chemicals often relies on the carbon structure of fossil resources. A sustainable alternative source of this carbon structure is biomass, a collective name for plant and animal material. Since lignocellulose is the most prevailing form of biomass and widespread, it is an interesting carbon feedstock.

1. Lignocellulose composition

Lignocellulose is the main constituent of plant cell walls, and it mainly functions as a structural component. It is a complex matrix of three main entangled biopolymers¹:

- cellulose (30-60%);
- hemicellulose (10-40%);
- lignin (10-30%).

Since lignocellulose has a biological origin, its composition and structure vary depending on the source, growth condition, age, etc. Plants are often divided in three main groups being hardwoods, softwoods and grasses and their lignocellulose composition is distinct.

Cellulose

Cellulose is the main biopolymer of lignocellulose, and it is exclusively composed of D-glucopyranose units which are linearly linked via β -1,4-glycoside bonds. The linear homo-polysaccharide chains (degree of polymerization up to 10000) interact with each other via intra- and inter-unit hydrogen bonds and VDW forces. Several linear chains form a structure with rigid crystalline and flexible amorphous zones, resulting in a semi-crystalline macrostructure. These fibrillary structures are insoluble in a lot of solvents (e.g. water) and have a high tensile strength, resulting in both a high chemical stability and mechanical strength of a plant cell wall.¹

Hemicellulose

In contrast to cellulose, hemicellulose is a branched heteropolysaccharide consisting of both pentoses (e.g., xylose and arabinose) and hexoses (e.g., mannose, galactose, and glucose). It often contains uronic acids (e.g., glucuronic acid) and acetyl moieties as side-side groups. The chemical composition varies among others from the botanical origin. Typically, hardwoods have a backbone of D-xylose units (e.g., glucuronoxylan) whilst softwoods can have a backbone of D-xylose, D-glucose, or D-mannose. The resulting polymeric structure (d_p up to 300) is amorphous. Consequently, it is easily solubilized and depolymerized in mild acidic conditions. In the plant cell wall, hemicellulose connects cellulose microfibrils and together with other carbohydrate polymers (e.g., pectins), it forms

holocellulose. Furthermore, it plays a pivotal role in the construction of lignin-carbohydrate complexes (LCC).¹

Lignin

Lignin is the third structural component of lignocellulose and is considered as being structurally complex. It reinforces the cell wall, enables water transport and acts as a physical barrier to pathogens. Lignin is an amorphous aromatic polymer formed by a radical polymerization of oxygenated phenolic monomers - monolignols - in the plant cell wall. Originating from phenylalanine and tyrosine (in grasses), they are synthesized in the phenylpropanoid pathway. Typically, those monolignols are *p*-coumaryl, coniferyl and sinapyl alcohol mixed with various other aromatic monomers. To date, 35 different monomers have been discovered in natural lignins. The composition of lignin varies among distinct species, individuals of the same species and even within individual species (e.g., heartwood, sapwood).^{2,3}

After a heavily regulated transport to the plant cell wall^{2,3}, laccase and peroxidase enzymes oxidize (dehydrogenation) the phenolic hydroxyl group. The resulting phenoxy-radical is stabilized by resonance. Lignification occurs when two radicals (at position 4-O, 5 or β) couple via a purely chemical process (no regulation). This polymerization - predominantly endwise -eventually produce a racemic polymer with different types of inter-unit linkages.

Since the radicals at position 4-O and β are most reactive, the β -O-4 - A - ether inter-unit bond is most abundant (50-80%). Other ether bonds originating in lignification are the 4-O-5 bond – E - and the α -O-4, α -O- γ , α -O- α and 4-O- β , yet the latter four ether linkages are always in combination of a more resilient C-C inter-unit bond in natural lignin. These C-C inter-unit structures are phenylcoumaran – B - (β -5, α -O-4), resinol - C- (β - β , 2x α -O- γ), dibenzodioxocin - D- (5-5, 4-O- β , α -O-4) and spirodienone – F – (β -1, α -O- α). Other structures such as triclin and ferulic acid are incorporated in the lignin-structure as well. As with the various monolignols, the relative distribution of the inter-unit linkages varies significantly with botanical origin, individual species, age, growth conditions, etc. ^{2,3}

One crucial factor governing the relative distribution is the S/G/H ratio of monolignols. Since syringyl moieties bear a methoxy group on both position 3 and 5, radical coupling cannot occur on position 5, hampering the synthesis of β -5, 5-5 and 4-O-5 inter-unit bonds. Hardwood lignin has a high content of S-units (50-80%), often resulting in a β -O-4 content over 60%. Softwood lignin on the other hand is predominantly composed of G-units. Consequently, it contains a lower β -O-4 content (up to 50%) and more C-C inter-unit bonds.¹

2. From lignocellulose to bio-aromatics: conversion strategies

Many studies have shown that lignocellulosic biomass holds enormous potential for sustainable production of chemicals and fuels, and more specifically bio-aromatics. Aromatics represent a significant share of today's chemical building blocks, which are currently virtually all made from fossil oil.

The most important constituent in lignocellulosic biomass for production of bio-aromatics is lignin due to its high functionalization (see §0). However, the full potential of lignin for commodity polymers is recently underutilized, mainly due to the difficulty in obtaining aromatic chemicals from lignin. Therefore, research on lignin deconstruction became the last years the center of interest for scientists and companies worldwide. Multiple processes with varying process conditions have emerged. These processes can be divided into two conversion categories, including a two-step strategy in which lignocellulosic biomass is firstly fractionated and secondly depolymerized, and a one-step strategy directly converting lignocellulosic biomass into bio-aromatics.

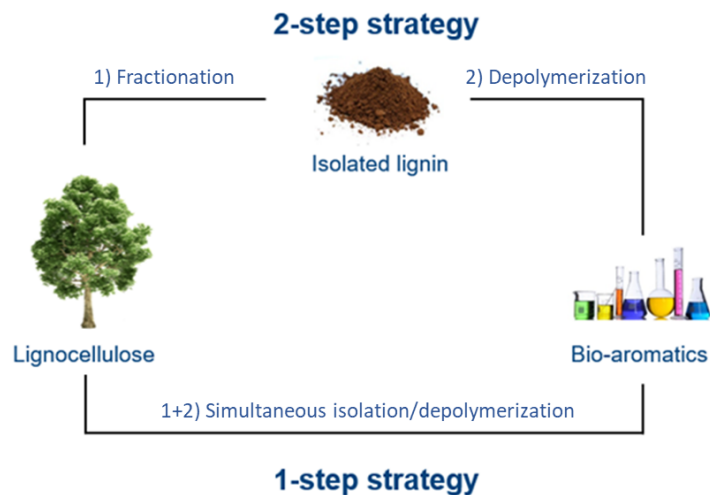


Figure 1: Schematic overview of lignocellulose conversion strategies

An overview of the different fractionation, simultaneous isolation/depolymerization and separate depolymerization technologies is given in respectively chapters 2, 3 and 4.

3. Availability of lignocellulosic biomass

Adequate volume of biomass, a reliable supply chain and free trade are three essential pillars for the development of a biobased economy. Therefore, a feedstock supply inventory was set up within the BAFTA project. This inventory provides comprehensive qualitative and quantitative data on a selection of feedstocks that are potentially suited to produce biobased aromatics including different types of lignin, virgin wood, waste wood and flax. A summary of the quantitative data available on virgin wood is presented in Table 1.

Table 1: Availability and price of different types of virgin wood

Feedstock subtype	Average price (EUR/ton)		Mass dry (ton/year)	
	Flanders	World	Flanders	World
Round wood – Coniferous/softwood	32	49	± 130 000	± 600 000 000
Round wood – Non-coniferous/hardwood	42	48	± 125 000	± 400 000 000
Poplar	89		± 100 000	± 30 000 000
Firewood/wood fuel	13		± 250 000	± 900 000 000

Based on the qualitative sheets containing data on geographical location, market players, contractibility, price trends, current users, sustainability and processing, following conclusions could be made:

- The lignin market is an emerging market. The number of players is limited and highly concentrated, with top ten players accounting for more than 90% of the global market in 2015. Currently, lignin is mainly used for energy production.
- The virgin wood market is established worldwide. High volumes of virgin wood are available. There are many players on the market. Forest industry is segmented into the pulp and paper industry and the wood industry. Biggest part of virgin wood is used for material purposes.

The waste wood market is established in the EU. It has a strong international focus with trade of waste wood between (often neighbouring) countries. Waste wood is used for energy purposes and material applications.

For lignin, an update of availability and price was made within the Nibcon project with a focus on hydrolysis lignin and organosolv lignin. Data were gathered from companies' websites and online reports, as well as a questionnaire that had been performed by VITO in the past.

Hydrolysis lignin is a byproduct of biomass processing in the production of bioethanol, while organosolv lignin is a byproduct of a refinery in which the organosolv process has been implemented to extract lignin from lignocellulosic biomass. Most refineries are still in pilot phase and therefore, the availability is estimated based on the assumption that each biorefinery in Europe will reach a capacity of 40 000 tons of wet lignin cake per year. In that case, 350 tons of organosolv lignin and 4 200 tons of hydrolysis lignin will be available in Europe per year.

Since no lignin market exists yet, prices for the lignin are determined based on values found in the literature and based on personal communication with lignin providers. Prices for organosolv lignin range from 250-750 EUR/ton, while the hydrolysis lignin price is set between 80-450 EUR/ton. The wide range in reported prices is due to the different price setting strategies. In some cases, the price is estimated based on for example the energy value, whereas in other cases it is based on the production costs or the estimated value on the market considering the targeted applications.

Chapter 2: Lignocellulose fractionation

The lignocellulose matrix contains many interesting molecules to produce chemicals and materials. Yet, the three main biopolymers are intertwined into a complex structure. Accordingly, lignocellulose is often fractionated in a biorefinery prior to further downstream processing of each product stream to marketable products. Due to the large variation in lignocellulose composition and potential targeted products, many biorefinery schemes have been developed, each with their benefits and drawbacks. An optimal biorefinery that facilitates the exploitation into all potential end-applications does not exist. One rule applies to all strategies: fractionation determines the properties and thus the application potential of the individual lignocellulose constituents.

In the following section, an overview is given of interesting lignocellulose fractionation methods with a focus on the lignin product outcome.

1. Kraft process

Most contemporary lignocellulose biorefineries mainly focus on the valorization of the cellulose fraction, imposing quality standards to the refined cellulose product. Kraft pulping is in this context the principal commercial process to fractionate lignocellulosic biomass and has been optimized to deliver a cellulose-based product which meets the demands of the pulp and paper industry.⁴

In conventional Kraft mills the feedstock and white liquor, an aqueous solution containing both NaOH and Na₂S, is loaded into the reactor vessel. The liquor is heated to a cooking temperature of 155-175°C for a few hours depending on the feedstock, temperature, and desired degree of delignification.⁶ During the process, lignocellulosic biomass is subjected to a base catalyzed depolymerization by hydroxide and hydrosulfide anions. In this alkaline reaction medium, lignin molecules are deprotonated, strongly increasing their solubility, and hampering lignin deposition on the pulp.^{5,6} Ultimately, the process results in the formation of a black liquor. This is a mixture of soluble lignin and carbohydrate degradation products, from which lignin can be isolated by precipitation after neutralization with an acidic solution. However, Kraft lignin is rarely recovered. Usually, the black liquor is incinerated to (i) regenerate the pulping chemicals and (ii) generate energy and electricity.^{1,4,7}

The addition of both NaOH and Na₂S results in a unique interplay of HS⁻ and OH⁻ ions. Briefly, these ions readily cleave the most common interunit linkage, *i.e.*, the β-O-4 bond, at temperatures of around 150°C. Both phenolic units and non-phenolic units are depolymerized, the former being the most reactive. The phenolic units transform into a quinone methide and tend to react with strong nucleophiles such as the carbanions from the phenolic structures or sulfide anions. Via a complex network of depolymerization and condensation reactions, ultimately a sulfur-containing, highly condensed lignin structure is obtained. The homogeneous catalysts are regenerated by incinerating the black liquor and by treatment with sodium carbonate and calcium hydroxide.^{1,4,5,7,8}

During kraft pulping, the native lignocellulose is subjected to harsh reaction conditions. The result is a relatively pure cellulose-enriched pulp (over 90% delignification) and a condensed high Mw lignin containing 1-3% sulfur. Almost all the native β-O-4 and α-O-4 bonds are eliminated. This deficiency, combined with the high molecular weight and the presence of a substantial amount of sulfur, a known catalyst poison, impedes further valorization of kraft lignin, especially regarding aromatic chemicals. On the other hand, the residual cellulosic pulp is of excellent quality for upstream processing in the paper industry.^{4,9,10}

2. Sulfite process

The sulfite process used to be the dominant process to produce cellulosic pulps from lignocellulose. Because of the development of the more profitable Kraft process the global use of the sulfite process decreased significantly. Nevertheless, the process still creates commercially available lignosulphonate products, used in a variety of applications.^{1,11}

Generally, the biomass is brought in contact with an aqueous solution of a sulfite salt (Na^+ , Mg^{2+} , Ca^{2+} or NH_4^+ salts of SO_3^{2-} or HSO_3^-). The type of salt determines whether lignocellulose is treated under acidic, neutral, or alkaline conditions. During the reaction time of 1-5h, the following events happen: (i) lignin-hemicellulose bonds are broken, (ii) lignin and part of the hemicellulose are released from the lignocellulose matrix, (iii) hydrolysis, sulfonation and condensation reactions of lignin and hemicellulose occur. The product outcome is a mixture of condensed sulfonated lignin, sugar derived products and extractives.^{5,6,11,12}

The type of salt and its concentration determine the chemical regime.¹¹ An acidic environment (pH 1-2) is required when using calcium sulfites, whereas magnesium sulfites must be operated in a pH window of 4-5. Sodium and ammonium sulfites on the other hand do not have any pH constraints, making both acidic and alkaline operation possible. In general, the operating temperature of an acidic pulping environment is lower than a neutral-alkaline (125-145°C vs. 150-175 °C).^{5,6,13}

In acidic conditions, benzylic carbenium intermediates are formed by loss of hydroxyl groups. These intermediates are prone to a nucleophilic attack. Thus, the intermediate can be sulfonated at the α -C position. On the other hand, nucleophilic sites at phenolic rings compete with the sulfite ions, generating new C-C bonds.^{1,5,10,14} At neutral or alkaline pH, quinone methide structures are formed in an analogous way as during the kraft process. Those are also prone to nucleophilic reactions of sulfite ions and condensation reactions.^{5,10,11}

The residual pulping liquid will always comprise a mixture of lignosulfonates, depolymerized hemicellulose products and extractives.^{11,14} The amount of delignification can be finetuned by an interplay of the pH and temperature, as well as by multistage cooking.^{5,11,14} During sulfite pulping, 4-8% of sulfur is incorporated in the lignin structure. This makes the lignin water-soluble and prevents redeposition on the pulp fibers.¹⁴ In contrast to Kraft lignin, sulfite lignin is typically less deconstructed resulting in a higher molecular weight. Despite this higher M_w , the sulfite process effectuates a considerable decrease in the β -O-4 content and a relative increase of C-C bonds. Their isolation from the process liquor is challenging due to their water solubility. Lignosulfonates have various applications such as emulsifiers, dispersants and adhesives due to their solubility in water.^{1,6,10,15,16}

3. Soda process

The soda pulping process originates in the 19th century and is closely related to Kraft pulping. It is industrially being used for processing non-woody biomass, *i.e.* herbaceous crops, since this type of biomass has a more accessible structure and therefore doesn't require harsh Kraft pulping conditions.^{6,12,17}

Typically these herbaceous crops, which are for instance agricultural waste such as wheat straw or sugarcane bagasse, are mixed with an aqueous NaOH solution (approximately 1M). The mixture is then heated to 160-170°C for 1-4 hours during which the following base-catalyzed events take place: (i) cleavage of lignin-carbohydrate bonds, (ii) breaking the β -O-4 interunit lignin bonds and solubilization of the lignin (iii) further depolymerization and condensation reactions. Also the hemicellulosic structure undergoes a range of reactions, including depolymerization via hydrolysis and subsequent solubilization and degradation of the released sugars. Diffusion and extraction of hemicellulosic and lignin derived products occurs more easily in comparison with woody biomass because of the more

open structure of the cell wall in non-woody biomass. After filtration of the pulp, a residual pulping liquor is obtained.^{4,6,12,17}

The alkaline environment, resulting from NaOH, catalyzes the deprotonation of the α -OH of non-phenolic β -ethers. The anionic intermediate is prone to epoxide formation, causing the β -ether to break. Hereafter, several reactions take place including the production of a quinone methide intermediate, the elimination of a γ -OH as formaldehyde resulting in an alkali-stable enol-ether, and a complex network of repolymerization reactions.^{1,4,6} A popular additive to soda pulping is anthraquinone (AQ). This improves the delignification of biomass whilst retaining more hemicellulose in the pulp.¹⁸ It is hypothesized that AQ works as a redox shuttle: (i) it oxidizes the aldehyde end groups of carbohydrates to carboxylic acids, eventually generating AHQ²⁻. The carboxylic acids impede hemicellulose loss. (ii) AHQ²⁻ is regenerated through the reductive cleavage of β -O-4 linkages, improving the delignification.^{19,20}

The residual pulping liquor contains a mixture of low and high molecular weight lignin fragments, solubilized and degraded sugars from hemicellulose and extractives.^{9,17} The lignin products can be recovered by precipitation and filtration and have a lower M_w lignin than for instance Kraft lignin.^{9,18,20} The lignin stream is also characterized with a low amount of β -O-4 content and a relatively high amount of C-C bonds indicating a condensed structure.^{9,17} It has to be stressed that soda lignin is sulfur free in contrast to Kraft lignin and sulfite lignin. This creates more opportunities for subsequent processing.

4. Ammonia processes

The use of ammonia in biomass fractionation is attractive for various reasons (viz. nature of interactions, solvent capabilities, cost, volatility, availability,...). Therefore several ammonia based processes were developed in the previous decades. Most ammonia pretreatment publications cover ammonia fiber expansion (AFEX) but also anhydrous ammonia pretreatment (AAP) and ammonia recycle percolation (ARP) are being studied. Common features (besides the use of ammonia) are the alkalinity and mild temperature of the process and a relatively high degree of structural preservation of the lignin structure.

Ammonia fiber expansion

Ammonia fiber expansion is typically performed with moist biomass loaded in a reactor together with liquid ammonia (0.3-3g NH₃/g dry biomass). Technology for different reactor set-ups has already been developed, including batch, screw type, packed bed and fluidized bed reactors.²¹ As a result of the exothermal reaction between ammonia and water, the reactor is heated to the desired temperature (60-160°C), which is maintained for maximum 1 hour.^{1,21-23} Several events occur during processing including: (i) penetration of ammonia in the biomass causing it to swell, (ii) a partly alteration of the cellulose crystal structure due to OH-N bond formation, (iii) reaction of ammonia with water and formation of ammonium hydroxide, (iv) ammonolysis and hydrolysis of the lignin-hemicellulose ester bonds and (v) dissolution of lignin and hemicellulose. Afterwards, the pressure is rapidly released, causing the evaporation of NH₃, redeposition of lignin and hemicellulose on the exterior cell walls and a decompression of the biomass, thereby improving the accessibility of cellulose.^{1,21-26}

Ammonia has a critical temperature of 132°C and a critical pressure of 113 bar. Thus depending on the process conditions, ammonia is in its (sub)critical state. The high reaction pressure and pressure swing in AFEX impose specific requirements on the reactor equipment.^{21,27} Another important factor is the recovery of ammonia, since a part of it is chemically incorporated into the biomass components.

However, it is postulated that over 98% of the ammonia is theoretically recoverable.^{23,27}

Since AFEX is a pretreatment method developed for the subsequent conversion of the carbohydrate fraction, research has mainly focused on the retention and structural availability of cellulose and hemicellulose. AFEX does not hydrolyze hemicellulose to soluble sugars, nor does it extract lignin.^{23,28} Nevertheless AFEX causes a redistribution of those components within the cell wall, which allows the isolation of up to 65% of lignin *via* a subsequent extraction. This extracted lignin has a relatively high degree of structural preservation, though a reduction in dibenzodioxocin units, ferulate and p-coumarate bonds and β -O-4 interunit bonds has been observed.^{29,30} Furthermore some nitrogenous degradation products such as phenolic amides and maillard reaction products are formed.^{23,25}

Anhydrous ammonia pretreatment

Anhydrous ammonia pretreatment (AAP), also called extractive ammonia pretreatment (EAP) has two big dissimilarities with AFEX: (i) the biomass requirements and (ii) the recuperation of ammonia. AAP imposes more stringent requirements to the biomass since the moisture content should be less than 10 wt%. In analogy to AFEX, the feedstock is fully emerged in liquid ammonia, but since little water is present in the 'dry' biomass, only a limited amount of exothermic heat is released by the formation of ammonium hydroxide, hence requiring an exterior heat source to reach the required reaction temperature of 40-130°C.^{24,31-33} Liquid ammonia in the absence of water is known to be an excellent cellulose swelling agent. The ammonia penetrates the biomass and the OH-O hydrogen bonds in amorphous and crystalline cellulose are partially displaced by OH-N bonds. As a result an ammonia-cellulose complex is formed. If water is present, these bonds are formed to a lesser extent.^{24,34,35} Meanwhile, ammonolysis and hydrolysis of the lignin-hemicellulose bonds occur, followed by the dissolution and extraction of lignin out of the cell structure. In contrast to the explosive pressure release of ammonia in AFEX, an external overpressure is applied, isolating the liquid ammonia and its solutes from the cellulosic pulp, whose crystal structure alters from the natural cellulose I polymorph to the cellulose III polymorph.^{23,24,31-33}

Since ammonia is a volatile component, equipment is necessary to withstand the high operating pressure (< 100 bar). Furthermore, an inert gas has to be present at high pressure to exert an overpressure, facilitating the removal of liquid ammonia and its solutes. Ammonia can be recovered by evaporation, after which it has to be liquefied again to start a new run.^{27,33}

The brown viscous liquid obtained after ammonia evaporation contains the extracted lignin and little degradation products of hemicellulose.³¹ Since AAP is a relatively mild fractionation method, only a part of the lignin is extracted (<50%) sharing various characteristics with native lignin such as a relatively high β aryl ether content. During the process, ammonolysis of ferulate and coumarate esters generates the respective amide derivatives feruloyl amide and p-coumaroyl amide.^{24,28,32,33} The obtained pulp with the cellulose III polymorph is more prone to enzymatic hydrolysis than native cellulose polymorphs.^{24,32}

Ammonia recycle percolation

Ammonia recycle percolation (ARP) is the best ammonia-based process in terms of lignin extraction yield. The lignocellulosic biomass is loaded in a fixed bed reactor, over which a continuous flow of aqueous ammonia (5-15 wt%) is sent at a temperature of 140-210°C.^{27,30,36-40} Aqueous ammonia, or ammonium hydroxide⁴¹, is known to cleave the lignin-hemicellulose bonds resulting in the release and solubilization of lignin. In batch set-ups the solubilized lignin components have the chance to repolymerize and redeposit on the cell wall structures. This problem is circumvented in ARP due to the

sufficiently rapid flow of aqueous ammonia, which facilitates the extraction and evacuates the soluble lignin fragments out of the reactor, allowing their isolation from the fixed pulp fraction in higher yields. Common reaction times are 0.25-2h.^{27,36-38,41}

The reactor compartment is pressurized to 20-25 bar with an inert gas to prevent flash evaporation of ammonia when arriving at the heated reactor zone. After percolation of the aqueous ammonia solution through the lignocellulose bed, it ends up in a second reactor compartment (without biomass). In here, a continuous flash evaporation of ammonia allows the recuperation of the gas after which it is condensed and reused.^{30,36,42}

The percolation principle minimizes repolymerization and redeposition of lignin allowing high lignin extraction yields (75-85%), which is the main advantage of ARP.^{27,36-38,43} This extract is associated with a lot of hemicellulose derived products (up to 50%)^{36,37} yet a more purified lignin precipitate can be obtained. The precipitate contains little nitrogen and a relatively high amount of ether bonds.^{31,43} In the residue a cellulosic pulp is obtained with over 90% of glucose retention. In contrast to AAP the cellulosic crystal structure isn't altered, due to the aqueous environment.^{37,39}

5. Acidic Flow-Through

Dilute acid pretreatment (DAP) and hot water pretreatment (HWP) are two closely related fractionation technologies. In both cases the reaction medium promotes acid catalyzed depolymerization reactions. A flow through (FT) set up is of vital importance to isolate lignin, because it avoids lignin repolymerization and deposition on the solid cellulose pulp.

In DAP-FT, the biomass is loaded in a fixed-bed flow-through reactor together with a mineral acid (H_2SO_4 is mostly applied) in low concentrations (0.05-2 wt%) and heated to a temperature between 120-200°C. In HWP-FT, no mineral acid is added and the acidity in the reaction medium originates from both water dissociation - pK_w shifts at higher temperature - as well as the acids released from the biomass (e.g. acetic acid). Since HWP-FT has no additional added acids, the required operating temperature is higher than that of DAP-FT (160-240°C).⁴⁴⁻⁴⁷ Taking into account both acidity and temperature, the flow rate needs to be adapted. For this reason required reaction times vary between minutes up to a few hours for high or low severity process conditions, respectively.^{47,50,51} Common operating pressures are up to 25 bar.^{46,47} The mild acidic environment promotes several reactions: (i) cleavage of the lignin-hemicellulose bonds, (ii) breakdown of the hemicellulose polymer resulting in short oligomers and C5 and C6 sugars (iii) partial depolymerization of the α -O-4 and β -O-4 bonds, generating reactive intermediates, (iv) repolymerisation reactions of the released lignin fragments and fast extraction of the solubilized sugars and lignin from the reaction medium due to the flow-through set-up.^{1,44-48}

The obtained aqueous product stream contains a mixture of depolymerized hemicellulose (short oligomers, monomers and degradation products such as furfural)^{46,48} and solubilized lignin. The degree of delignification is determined by a lot of parameters including the acidity, temperature and flow rate.^{46,48} Up to 75-85% lignin yield can be obtained under optimized conditions^{46,49,50} Since the acidity of HWP-FT is lower, the remaining pulp will typically be less delignified.^{44,45} Some β -O-4 bonds are preserved because of the mild acidic conditions under flow-through regime.⁵¹ The yield of the aromatic monomers such as vanillin, syringaldehyde, coniferylalcohol and sinapylalcohol is rather low.^{52,53} Since precipitation of oxygenated low molecular weight molecules is difficult, the complete isolation of the extracted lignin is challenging.

6. Pyrolysis

Although most studies concerning pyrolysis starts from isolated lignin, pyrolysis of lignocellulose materials is also well-known. The lignocellulosic biomass is heated in the absence of oxygen and solvents to the desired high temperature of 400-600°C. The applied heating rate and residence time determine whether the process is termed pyrolysis or fast pyrolysis. Conventional pyrolysis has a heating rate in the order of 50°C/s and a residence time of 5-30 minutes whilst fast pyrolysis has heating rates of about 1000°C/s and a residence time in the order of seconds. Since the residence time is very short, mass transfer and heat transfer phenomena play a critical role imposing limits to the particle size of the lignocellulosic biomass. During pyrolysis, thermal reactions form gasses and vapors, which are immediately quenched after the heating zone. Eventually three products are generated: gases, char and bio-oil, the latter containing a complex mixture of aromatic components.⁵⁴⁻⁵⁸

In traditional pyrolytic systems, no catalyst is added. Nevertheless different chemical events take place under influence of the required high temperature. The first significant mass loss occurs at 220-315°C when hemicellulose starts to decompose. A lot of different products including furans, pyranones, acids and ketones are generated. Due to its crystalline structure, cellulose starts to decompose at a higher temperature (315-400°C) forming a myriad of products. Lignin is even more difficult to decompose because of its heterogeneity. In a wide temperature range of 150-900°C lignin-derived products are being formed. For instance, at 150-300°C the α and β aryl ether linkages of lignin are broken, dehydration of lignin starts at around 200°C and the aliphatic side chains start to split at 300°C.⁵⁴⁻⁵⁶ Finetuning of the process parameters is critical since a too low temperature and too long residence time favor the production of charcoal whilst a too high temperature increases the biomass conversion to gas. A short residence time combined with an adequate temperature of around 500°C maximizes the bio-oil yield comprising the desired aromatics.⁵⁶

A dark brown bio-oil can be obtained in 70-75% yield by fast pyrolysis.⁵⁷⁻⁶⁰ The bio-oil contains a numerous of molecules including cellulosic, hemicellulosic and lignin-derived degradation products. Moreover, the crude bio-oil has a water content of 20-30%.^{57,58} Typical pyrolysis oils are characterized by high acidity, low heating value, high viscosity, and chemical instability.^{54,55,57,58,60,61} Up to 15% of the bio-oil are lignin-derived aromatic products, which are a mixture of monomers and short oligomers with a relatively high oxygen-content that primarily comprise C8 unit skeletons rather than the C9 phenylpropane subunits typically found in native lignin.^{57,62-64} If this complex unstable oil is ought to be useful, upgrading is of the utmost importance. This can be done ex situ or in situ. During in-situ upgrading, the vapors are led through a catalyst bed for further conversion in stable, oxygen depleted components. A lot of catalysts can be applied (zeolites, metal oxides, supported metals,...) promoting several reactions including cracking, aromatization, ketonization, hydrodeoxygenation and steam reforming.^{54,55,65}

Another upgrading possibility is the liquid-phase separation of pyrolysis-oil with water, rendering water-soluble sugars, sugar derived products and low molecular weight phenolics. The water-insoluble residue contains mainly lignin derived molecules: 'pyrolytic lignin'. The low M_w oligomers are characterized by newly formed C-C linkages and a strong depletion in aryl ether linkages.⁶⁶⁻⁷⁰

7. Solvolytic

An extensive amount of academic research has been performed on organosolv based processes in the past decades. A large asset of this technology is the possibility to valorize the three main lignocellulosic building blocks towards chemicals.^{4,71,72} In a typical organosolv strategy, the biomass is loaded into a reactor together with a water/solvent mixture and often also a homogeneous acid. The reactor is heated to a temperature of 100-270°C for a reaction time of 0.05-4h, depending on the desired process severity. Following events occur during reaction: (i) interunit lignin bonds (α -O-4 and β -O-4) are cleaved as well as the lignin-hemicellulose ether and ester linkages, resulting in a solubilized lignin that can be extracted from the lignocellulose matrix, (ii) the solubilized lignin undergoes further depolymerization through more extensive cleavage of the α -O-4 and β -O-4 bonds, hereby generating

reactive intermediates, (iii) these intermediates have the tendency to repolymerize, creating condensed structures (new C-C bonds), (iv) the glycosidic bonds of hemicellulose are cleaved, resulting in the production of water-soluble low M_w sugar-derived products. After reaction, the residual pulp is separated from the liquid products (containing solubilized lignin and hemicellulose). Often, the liquid products are subsequently diluted with water, resulting in the precipitation of lignin.^{1,4,71-73}

Common applied solvents in organosolv processes are mixtures of water with short primary alcohols (e.g. methanol^{74,75}, ethanol^{76,77}, butanol⁷²), cyclic ethers (e.g. furfural⁷⁸, dioxane⁷¹, 2-methyltetrahydrofuran⁷⁹⁻⁸¹) or ketones (e.g. acetone⁸²). The water/solvent ratio is an important factor, since it influences the acidity and the solubility parameter. The latter should be around $11 \text{ cal}^{1/2}\text{cm}^{-3/2}$ in order to effectively solubilize low and high molecular weight lignin fractions.⁷¹ Moreover the boiling point is determined by the water/solvent ratio, which has an inversely proportional effect on the ease of solvent recovery and the cost associated with high pressure equipment. Other parameters to consider when selecting the solvent are its cost, availability and handling safety.

The solvolysis can occur with or without added homogeneous catalyst, in the latter the reaction proceeds *via* autocatalysis due to the presence of hot water and released acids from biomass. Either way, lignin undergoes acid catalyzed depolymerization and condensation reactions, resulting in oligomeric fragments.^{4,71,83} The advantage of the autocatalytic system is that fewer 'phases' are present in the reaction medium, simplifying downstream processing. On the other hand, the required reaction conditions in terms of temperature, pressure and residence time are typically harsher since the acidic environment is less severe. Introducing more acidity by adding a homogeneous inorganic acid (e.g. H_2SO_4 , HCl) or organic acid (e.g. formic acid, acetic acid) lowers the severity of the required reaction conditions (lower T, P, t) since it facilitates the solvolytic reactions.^{4,71,83}

The product outcome is strongly intertwined with the acidity of the environment. It is well described that in a strong acidic environment lignin is prone to undergo repolymerization reactions. Those repolymerization reactions are accelerated by the acid catalyzed elimination of interunit γ -OH groups as formaldehyde, eventually resulting in additional C-C crosslinks in the form of diphenylmethane structures. The rate of those reactions is particularly high at $\text{pH} < 2$ and lower between $\text{pH} 2-7$, the latter resulting in a lignin product with more retained aliphatic OH-groups and a lower molecular weight.^{4,72,83} Furthermore, in less severe conditions the β -O-4 bond can be (partly) preserved, in turn facilitating lignin depolymerisation in a subsequent step. However this is often accompanied with a lower amount of delignification, which at least partially counteracts the increased depolymerisation efficiency of the obtained organosolv lignin.^{1,71,84}

8. Stabilisation agents

A general challenge during wood fractionation is the trade-off between delignification and repolymerization. A high delignification yield typically requires harsh process conditions, causing undesired repolymerization reactions. Conversely, a high structural preservation requires mild process conditions, resulting in low lignin yields. This issue can be tackled by stabilizing the reactive intermediates, thus impeding undesired repolymerization. This strategy has been implemented by several technologies.⁸⁵

A recently reported solution was the combination of a regular acid catalyzed organosolv fractionation with the addition of a stabilization agent, resulted in a high delignification yield with a large amount of structural preservations.⁸⁶

In this innovative system, the biomass is loaded together with dioxane/water (9/1) as the solvent and HCl. As a stabilization agent, an aldehyde or a ketone is added. The reaction mixture is heated to mild temperatures (80°C) and is reacted for 1.5-5h. During the reaction, the stabilization agent actively

protects the β -O-4 bond through the formation of a 1,3-dioxane structure. This prevents the formation of reactive intermediates, typically occurring during conventional organosolv pretreatment, and subsequent repolymerization of those molecules.⁸⁵ Due to the acidic conditions, cleavage of the lignin-hemicellulose bonds and hydrolysis of the glycosidic hemicellulose bonds occur. After reaction, a product mixture containing non-condensed high molecular weight lignin and soluble carbohydrates and their degradation products is extracted from the biomass.^{86,87}

Initially, formaldehyde was used as the active stabilization agent. It reacts with the α -OH and γ -OH of the β -O-4 bond, resulting in a cyclic methylene acetal (1,3 dioxane structure). This prevents the acid catalyzed formation of the benzylic carbenium ion (starting from the α -OH) and subsequent depolymerization and repolymerization reactions. Moreover formaldehyde also protects reactive positions on the aromatic ring by the formation of hydroxymethyl groups, hereby limiting C-C coupling with those reactive positions.⁸⁶

Other stabilization agents with different functional groups (e.g. acetaldehyde, propionaldehyde, furfural, 2-butanone,...) can be applied as well. They all protect the α -OH and γ -OH by the formation of a cyclic structure (cyclic acetal, ketal or carbonate). Because those structures are less stable, the pretreatment conditions require finetuning depending on the applied agent. In contrast to formaldehyde, other stabilization agents do not react with the aromatic moiety, generating fewer structural alterations, which ultimately leads to a higher product selectivity after depolymerization. Besides reacting with lignin, the stabilization agent also interacts with the depolymerized hemicellulose (e.g. acetal protected xylose).⁸⁷

In case of the formaldehyde assisted stabilization, all non-reacted formaldehyde could be easily recovered by evaporation whilst the fraction incorporated as a protection agent usually is consumed during the subsequent depolymerization step.⁸⁶

This innovative approach eventually results in a delignification yield between 70 and 80%. The high amount of structural preservation in the extract, including the complete retention of the β -O-4 bond, provides a promising feedstock for subsequent upgrading. It has been proven that under reductive conditions, hydrogenolytic depolymerization of this isolated lignin results in near theoretical monomer yields of 50%, which corresponds to the monomer yields obtained with the one-step processes RCF and OCF. Moreover both the cellulosic pulp and the hemicellulose derived sugars are obtained in relatively pure form.^{86,87}

Chapter 3: One-step strategy: From lignocellulosic biomass to bio-aromatics

One-step strategies as reductive catalytic fractionation (RCF) and oxidative catalytic fractionation (OCF) enable both a high monomer yield and a high delignification yield with minimal repolymerisation. On the other hand, aldehyde-assisted lignin extraction combines a high delignification yield with a high structural preservation of the extracted lignin in its reactive polymer form.

1. Reductive catalytic fractionation

Reductive catalytic fractionation is a process first described in 1940 by Hibbert et al.⁸⁸ In the last five years this technology has emerged into the spotlight, since the elegant combination of fractionation, depolymerization, and stabilization allows high lignin oil yields combined with high monomeric yields.^{89–94}

The basic RCF-strategy comprises loading a lignocellulosic feedstock into a stirred batch reactor together with a heterogeneous redox catalyst, a solvent and a hydrogen source. The reactor is heated to a temperature between 180–250°C for a reaction time of 0.5–24h.^{4,95} During reaction, the following events occur: (i) ether and ester bonds between lignin and hemicellulose are cleaved together with a fraction of the labile β -O-4 interunit lignin bonds, allowing the release of lignin from the lignocellulosic matrix and solubilization in the solvent, (ii) once solubilized, β -O-4 and α -O-4 interunit lignin bonds are further deconstructed, which generates reactive low M_w intermediates, (iii) these reactive intermediates are reductively stabilized, thus preventing condensation and generating a stable mixture of substituted aromatic monomers and small oligomers. In contrast, the carbohydrate fraction in the lignocellulosic feedstock is largely retained during RCF, resulting in a delignified carbohydrate-enriched pulp.^{1,96}

The addition of a heterogeneous redox catalyst is the distinctive parameter between RCF and solvolysis. The role of noble (Pd^{90,97–107}, Ru^{89,94,102,106,108}, Rh^{106,109}, Pt^{106,109}) or non-noble (Ni^{92–94,96,110–116}, Cu¹¹⁷, Fe¹¹³) metals on a carbon or oxide support is to catalytically stabilize reactive depolymerization products. Crucial for this action is a good contact between the solid catalyst and the reactive intermediates in solution. This optimal contact can be achieved by applying a catalyst powder.⁹⁶ However industrial implementation of a catalyst powder seems impractical since it has the tendency to retain in the pulp, thus impeding catalyst recuperation and pulp valorization. To circumvent these problems, i) ferromagnetic catalysts such as Raney Ni⁹² or Ni/C¹¹⁸ ii) catalyst baskets using pelletized catalysts⁹⁹ or iii) a flow through fixed bed set-up with a separate biomass bed and catalyst bed were recently published^{119,120,126}. Especially in the latter two, optimizing the contact between the solubilized lignin intermediates with the catalyst bed is of utmost importance.

The chemical functionalities of the aromatic substituents can be fine-tuned by altering the operating conditions, the metal catalyst and the catalyst support. For example, using methanol as the solvent and carbon as the support material, palladium has the tendency to form products substituted with aliphatic hydroxyl groups (γ -OH) whereas ruthenium forms *n*-propyl substituents. On the other hand, nickel catalysts can produce both γ -OH deficient or enriched oils in methanol by varying the catalyst support or process conditions.¹

Co-catalysts such as inorganic acids (e.g. H₃PO₄¹⁰⁷), inorganic bases (e.g. NaOH¹⁰⁷), organic acids (e.g.

formic acid¹⁰⁴), salts (e.g. Ni(Cl₂)¹⁰³, NaHCO¹¹¹) or triflates¹¹⁹ are sometimes applied in RCF processes. Milder reaction conditions result from the addition of Lewis or Brønsted acids or base but in the latter the monomeric yield decreases significantly due to alkaline repolymerization chemistry.

Two disadvantages associated with the addition of a co-catalyst are: (i) an additional 'phase' is introduced in the medium, making the regeneration and downstream processing more difficult, (ii) corrosion resistant materials could be required, resulting in a higher CAPEX.

In order to reductively stabilize the reactive intermediates, a reducing agent (typically hydrogen) has to be present.¹ The most applied strategy is the addition of external hydrogen gas, however processes with hydrogen donating solvents (2-isopropanol) or with lignocellulose constituents functioning as the hydrogen source are known.^{92,100} The latter two have the advantage that no H₂-gas has to be introduced in the reactor resulting in lower operating pressures and a safer reactor environment but the reported monomer yields are often lower than in the case with H₂-gas. Moreover hydrogenation of the oxidized solvent is required to allow solvent recycling (e.g. isopropanol/acetone).¹

The best performing solvents in the RCF biorefinery are protic solvents with sufficient polarity. Short alcohols (methanol, ethanol, isopropanol, butanol, ethylene glycol) are most commonly used, sometimes in combination with water.¹ A crucial solvent parameter to consider is the boiling point. A higher volatility induces a higher autogenic reactor pressure, but on the other hand will facilitate the upstream solvent recovery. This solvent recovery is crucial to reduce OPEX costs and to isolate solubilized lignin and carbohydrate products. Interestingly, the addition of water to the organic solvent allows finetuning of the solvent polarity, protic nature and boiling point, resulting in milder reaction conditions. Another effect of the addition of water is the selective hydrolysis of the hemicellulose polymer towards sugar alcohols.^{98,106} Those are downstream separated by the liquid-liquid extraction resulting in the relatively pure fractionation of the lignocellulosic biomass in its three constituents.¹

Although certain process parameters, discussed previously, can be used as tools to influence the final lignin product distribution, for a large part the product outcome will be dictated by the choice of the lignocellulosic substrate. Briefly, hardwoods contain a higher amount of syringyl units, which increases the content of labile β-O-4 bonds, compared to softwoods and herbaceous crops. As a result, lignin oils originating from hardwood (up to 95% yield) contain a high selectivity towards low molecular weight molecules, often reporting monomer yields of >40%. In contrast to hardwood, softwood lignin is almost entirely constructed of guaiacyl structures, which are more prone to the formation of stable C-C bond crosslinks. Processing softwood will therefore typically result in a lower lignin oil yield (<70%) with fewer monomers (<25%) and more condensed higher M_w structures lacking the p-substituted syringyls. Interestingly the third possible feedstock class, herbaceous crops, contains a lot of p-coumaric acid and ferulic acid next to the common monolignols.^{1,120,121}

2. Oxidative catalytic fractionation

Oxidative catalytic fractionation of wood is a promising technology to convert lignocellulosic biomass into chemicals. It has an analogous integrated strategy as RCF, however oxidative conditions instead of reductive are applied.¹

In a typical reactor set-up, the biomass is loaded into the reactor and mixed with an aqueous alkaline solution (around 10% NaOH) and Cu(OH)₂ or CuSO₄·(H₂O)₅. The reactor is heated to the desired temperature (160-180°C) and molecular oxygen is added to the system (1-10 bar partial pressure). During the reaction time of 0.25-2h, the oxygen is partly consumed due to radical depolymerization

reactions. The depolymerized lignin product can be isolated by precipitation and extraction.¹²²⁻¹²⁴

The first studies concerning the oxidation of wood used an aqueous alkaline mixture with nitrobenzene as the oxidant instead of O₂. At 160-180°C the reaction lasted 2-4 h.^{122,124,125} Since the use of molecular oxygen as oxidant is particularly interesting (viz. low cost, high availability,...), following research was devoted to bypass its lower reactivity. It was found that in alkaline media the hydroxides of Ag(I), Co(III) and in particular Mn(IV) and Cu(II), which can also be applied as a sulfate, promoted the oxidation yield in a considerably shorter reaction time of 0.25-1h.^{123,126-128} The lignin is depolymerized by oxidative radical chemistry to a mixture of monomers and oligomers. The pH of the media plays a crucial role in determining the molecular weight. Though various hypothesized mechanisms exist, it is clear that a strong alkaline media is essential to obtain a high yield of aromatic aldehydes. Delignification also occurs at a milder alkalinity (e.g. pH 10) though without a substantial formation of aromatic monomers.^{123,129} The formed aldehydes aren't stable and are subjected to further oxidations to their corresponding carboxylic acid, which in turn can be further degraded, ultimately resulting in CO₂ and H₂O. In this radical environment also repolymerization reactions can occur. Tuning of the catalytic system is therefore of utmost importance.^{124,130,131}

The aqueous solution is heated to temperatures around 160-180°C, building up autogenous pressure. Due to the addition of molecular oxygen (1-10 bar partial pressure, depending on the conditions) at reaction temperature, the total reactor pressure is between 10-25 bar.¹²⁴

In the available studies on oxidative treatment of wood, near theoretical monomer yields (40-50% for hardwoods and 20-25% for softwoods) are reported using the alkaline nitrobenzene catalytic system. The aromatic aldehydes syringaldehyde and vanillin are the main products. The latter one can be obtained selectively starting from softwoods.¹²⁴ Similar product yields are obtained when using Mn¹²⁴ or Cu^{128,132} catalysts and O₂ as the oxidant. Strikingly, little information concerning the delignification and the oligomeric lignin structures has been found. Recently one study was published reporting almost complete delignification (>95%) of pine wood combined with a high cellulose retention (>85%) and a high vanillin yield (15-17%) using a CuSO₄(H₂O)₅ catalyst with O₂.^{124,128}

Chapter 4: Two-step strategy: Depolymerization of isolated lignin fraction

Most of the earlier described lignocellulosic fractionation methods result in polydispersed lignin mixtures of high molecular weight heteropolymers fragmented at varying degrees and with uncertain reactivity. Such mixtures are difficult to use, especially in the chemical industry which has a need for uniform and consistent raw materials. Therefore, a second step is required to convert the complex lignin compounds into small molecules for basic chemicals or oligomers for further application. The natural complexity of lignin however makes its depolymerization a challenging tasks. Multiple strategies have emerged, including chemical, thermal and biological depolymerization technologies (see Figure 2), whether or not using catalysts.

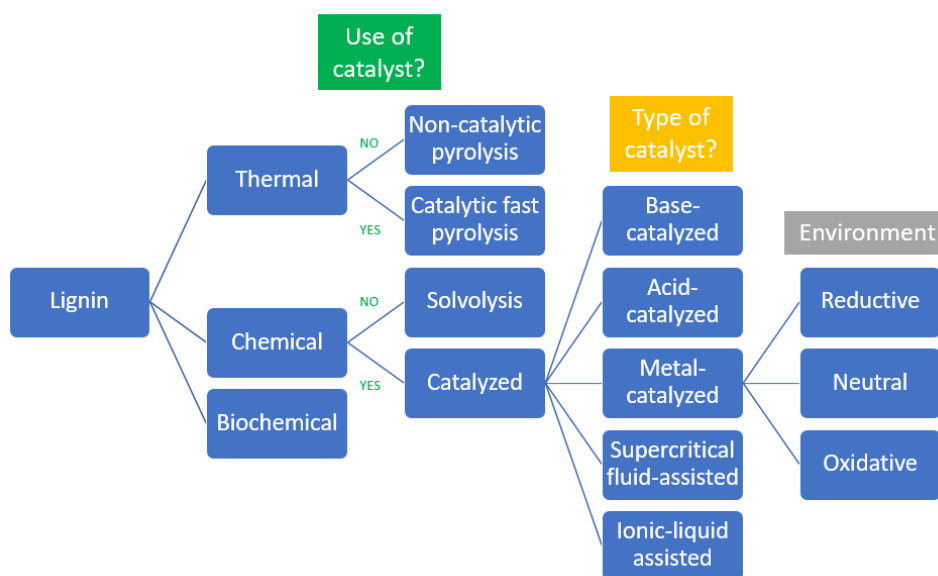


Figure 2: Categorization of lignin depolymerization processes

Within the next sections, a short description of the different technologies is provided.

1. Thermal depolymerization technologies

Fast and slow pyrolysis

Process description

Pyrolysis processes involve heating biomass feedstocks to temperatures between 400 to 700°C in an inert (oxygen-free) atmosphere. Thermal depolymerization of lignin results in the production of bio-oil, char (solid residue left after pyrolysis) and non-condensable gases. Bio-oil can be integrated into refineries as a raw material; char can be integrated into the pyrolysis process for reaction heat or sold for other purposes; the gas can be recirculated into the reactor to provide heat.¹³³ In contrast to other lignin depolymerization processes, pyrolysis does not require reagents and can be used either with the black liquor or with precipitated lignin.¹³⁴

Depending on operating conditions, the pyrolysis can be classified as slow pyrolysis (minutes to hours) or fast pyrolysis (seconds). The former is used for obtaining char as the main product (50-75% yield), bio-oil (15-20% yield) and non-condensable gases (20-30% yield). On the other hand, fast pyrolysis processes mainly produce bio-oil (50-70% yield).¹³³

Process conditions

Various parameters can influence the quality and yield of bio-oil, the most important being heating rate, particle size, reactor temperature and gas residence time. In order to achieve high selectivity towards the production of bio-oil, heating rates above 1000°C/min, particle sizes between 1 and 5 mm, reactor temperatures between 400 and 550°C and gas residence times less than 2s are required.^{59,133,135} According to Li et al., pyrolysis efficiency can be enhanced by using a good solvent.¹³⁶

Products

Next to the general remarks regarding product analysis in the introduction, a specific consideration should be taken into account in the case of pyrolysis. Vapor condensation results in re-polymerization reactions. This should be carefully considered when scaling up this technology. In some studies, the monomer content was analyzed directly from the pyrolyzer connected to GC-MS. Moreover, the pyrolysis was repeated off-line and the condensed vapors were again analyzed. In the latter sample, the formation of dimer and oligomers was observed.

Bio-oil derived by pyrolysis of lignin consists mainly of alkoxy-phenols and oxygenated aromatics (e.g., guaiacol, methyl guaiacol, syringol, methyl syringol, vanillin, syringaldehyde, vinyl syringol, vinyl guaiacol, 1,2,3-trimethoxy-benzene). The lignin-derived pyrolysis oil is more homogeneous compared to the bio-oil that derives from the parent lignocellulosic biomass, the latter consisting, in addition to the phenolic compounds, of various ketones, aldehydes, acids, furans, esters, ethers, alcohols, sugars and few aromatics and aliphatics. Such a phenolic bio-oil, derived from lignin, has greater potential of being utilized in the production of phenol-based resins substituting the petroleum derived phenol.¹³⁷

Catalytic fast pyrolysis

Process description

Typically, some kind of refining or upgrading step has to follow the depolymerization in order to modify the carbon, hydrogen to oxygen ratios to the preferred level. This downstream processing adjusts the product properties such as heating value, polarity or boiling point and hence the applicability with respect to biofuels or industrial bulk chemicals.¹³⁸

In the catalytic fast pyrolysis (CFP) of biomass the via thermal pyrolysis formed vapors of oxygenated oligomers and monomers (i.e., ketones, aldehydes, furans, acids, alkoxy-phenols, etc.) undergo in-situ deoxygenation (dehydration, decarbonylation, decarboxylation), cracking, isomerization, aromatization, condensation and oligomerization reactions on the catalyst surface.¹³⁷ High selectivity towards non-oxygenated aromatics (e.g. benzene, toluene) and alkyl phenols is obtained with catalytic pyrolysis. Catalytic upgrade is, therefore, essential for use of bio-oil as replacement of gasoline and diesel fuels.¹³⁹

Within catalytic fast pyrolysis, the catalyst serves a dual role. On one hand, the selectivity of the process shifts towards desirable and more stable products, while on the other hand repolymerization and coke formation reactions are avoided.¹³⁶

Process conditions

Besides the process conditions influencing the thermal pyrolysis process, also catalyst type and concentration are influencing the depolymerization process. The type of catalyst, including its porosity and acidity, influences the composition and yield of bio-oil.^{137,139} Mainly two types of catalyst are mentioned in literature, in particular zeolites and oxides.

Products

The addition of a catalyst favors the product distribution to valuable hydrocarbon compounds.¹³⁶ The lignin pyrolysis vapors composition is reflecting the initial lignin composition, meaning that pyrolysis bio-oil derived from, for example, softwood would mainly contain alkoxy-phenols with a single alkoxy group (guaiacol type), such as guaiacol, creosol, vanillin and eugenol.

In addition to the char formed in thermal (non-catalytic) pyrolysis of lignin, coke is also formed in the case of catalytic pyrolysis via condensation/polymerization reactions of phenols on the catalyst^{137,140} resulting in catalyst deactivation, which is one of the main challenges of the catalyzed pyrolysis process.¹⁴¹

2. Chemical depolymerization technologies

Base-catalyzed depolymerization

Process description

Base-catalyzed hydrolysis of lignin is seen as one exceptional route for the production of simple aromatic chemicals under mild conditions.¹³⁶ Lignin is depolymerized in the presence of a soluble or solid base, such as LiOH, NaOH and KOH. These catalytic reagents are cheap and commercially available.

Since aryl-alkyl ether bonds (including β -O-4 bonds) are the weakest bonds in lignin, cleavage of ether linkages is the dominant reaction in base-catalyzed depolymerization processes. According to Roberts et al., ether bonds are hydrolyzed at random, most likely from the outside of the oligomer, first forming larger units and then smaller subunits.¹⁴²

Process conditions

Product yield and selectivity are mainly determined by pressure, temperature, time, base concentration, base nature and lignin/solvent ratio.

In general, higher temperature, pressure and residence time result in higher depolymerization degree.

In order to cleave the ether linkages, a minimal temperature of 280°C is needed. Therefore, base-catalyzed depolymerization processes are often carried out at a temperature above 300°C. According to Li et al., a higher temperature and longer reaction time favor monomer generation.¹³⁶

Miller et al. studied the effect of base concentration and base nature.¹⁴³ Best results were obtained with strong bases like NaOH, and more specific with a molar excess of a strong base. Less insoluble products (unconverted lignin) were formed with increasing NaOH/lignin ratios.

Experiments were also performed in different solvents. Kinetics of reactions turned out to be faster in phenols or alcohols than in water due to the ether linkages solvolysis effect.

Products

Base-catalyzed depolymerization of lignin leads to a wide spectrum of products including oil, coke, residual lignin and gas. Bio-oil contains monomeric, dimeric and oligomeric aromatic compounds. According to Roberts et al., preferentially derivatives of syringol are formed, based on the stabilizing effect of the methoxy groups to the transition states of carbenium ions.¹⁴² A shift in product selectivity towards catechols and alkyl-catechols is observed at increasing temperatures.¹⁴⁴

In general, the number of monomers is rather limited because of (re)polymerization reactions of the formed products. Different strategies can be applied to minimize repolymerization and condensation reactions, as for example:

- the use of capping agents to capture reactive species (for example boric acid or formic acid);
- the use of more active catalysts to allow milder conditions;
- extraction of monomers before repolymerization occurs.

Acid-catalyzed depolymerization

Process description

Acid treatment of lignin is one of the most direct methods for depolymerization of lignin. Historically, acid pulping was mainly used for isolating lignin fractions from biomass, but more recently different types of acids have been tested for hydrolysis of lignin.¹³⁶

Within acid-catalyzed depolymerization processes, the dominant reaction is the hydrolytic cleavage of α - and β -aryl ether linkages. The lignin undergoes proton-catalyzed breakage of β -O-4 linkages to yield phenols, methoxyphenols and catechols.¹⁴⁵ Protons can be provided by different types of acid catalysts, including soluble Lewis acids, soluble Brønsted acids and solid Brønsted acids. Reactions can be performed in either water, an organic solvent, or solvent mixture.¹

Process conditions

Product yield and selectivity are mainly determined by pressure, temperature, time, acid concentration, acid type and lignin/solvent ratio.

In the 1940s, studies were performed at relatively low temperature (78 – 200°C), but at this temperature it was not possible to break the lignin polymer into monomeric compounds.¹⁴⁶ Nowadays, acid-catalyzed depolymerization processes are applied at a temperature above 280°C in order to be able to break the ether linkages. In general, highest yields and selectivities are reached under harsh conditions (high temperature and high pressure). At a temperature above 360°C, product selectivity is the highest and mainly methoxyphenols are formed.

Products

Acid catalyzed depolymerization of lignin leads to a wide spectrum of products including oil, coke, residual lignin and gas. Bio-oil contains monomeric, dimeric and oligomeric aromatic compounds. Main products formed are phenols, catechols and methoxyphenols. By rising the temperature from 360 to 400°C, product selectivity shifts towards methoxyphenols.

In general, the monomer yield is rather low (often below 20%). Main obstacle to increase this yield is the repolymerization of reactive intermediates. This can be avoided by trapping these intermediates, which is possible by acetal formation, hydrogenation and decarbonylation, of which especially the acetal formation route was found to be effective.¹

Metal-catalyzed depolymerization

Three different subclasses of metal-catalyzed depolymerization can be distinguished based on the presence of a hydrogen or oxygen donating solvent/catalyst and/or the use of hydrogen or oxygen gas, including neutral, oxidative and reductive processes.

Process description

Metallic catalysts are added to the system to increase the selectivity of lignin depolymerization. By introducing metallic catalysts, the activation energy of depolymerization is decreasing to a great extent, resulting in the possibility of using milder reaction conditions.¹⁴⁶

Metal-catalyzed depolymerization is studied in reductive and oxidative environment. According to Ahmad and Pant, distinction can be made between hydrogenation, hydrogenolysis, hydrodeoxygenation and oxidation.¹⁴⁵ The three first ones are reductive processes, all needing hydrogen which can be provided by an external source in gaseous form or in-situ via active hydrogen donating solvents (as for example formic acid). For the oxidation process, oxygen is required. Most often hydrogen peroxide is used as oxygen source, although oxygen can also be provided by an external source (as a gas).

Different types of metallic catalysts can be used. Studies are available on the use of:

- noble metals, including Pt, Rh, Ru and Pd;
- transition metals, as for example Cu, Zn and Ni;
- sulfur-containing metal catalysts;
- metal complexes in liquid state;
- heterogeneous bimetallic complexes;
- metal oxides.

The majority of metal catalysts used for reductive depolymerization can be applied for oxidation processes as well.

Homogeneous catalysts are difficult to separate from liquid products, therefore preference is given to heterogeneous catalysts. Solid catalysts are providing accessible metal sites at the external surface where the chemical reaction takes place and are thereby increasing the selectivity of the process. However, deactivation of these catalysts is clearly an issue but recyclability of the catalysts is barely mentioned in literature.

Process conditions

In general, metallic-catalyzed depolymerization processes can be applied at lower pressure and temperature compared to base- and acid-catalyzed depolymerization. Nevertheless, high cost and handling of high-pressure hydrogen system make it a complex process.¹⁴⁵ Use of in situ hydrogen or oxygen generation can overcome this obstacle.

In order to achieve the most desired products, increasing temperature and pressure are required to cleave aryl C-O bonds. Therefore, also reductive metallic-catalyzed depolymerization processes operate often at a temperature above 360°C.

Products

The type of products that is formed is depending on the reaction mechanism taking place. According to Ahmad and Pant, hydrogenation results in derivatives of methoxylated carbohydrates, while hydrogenolysis yields a wide range of value-added chemicals such as phenylpropanols, benzyl alcohols and aromatic oxygenates. Hydrodeoxygenation results into a complete removal of oxygen leading to the formation of aromatics and other cyclic compounds. Oxidative depolymerization assisted by metallic catalysts is leading to high-value chemicals such as vanillin, muconic acid and syringaldehyde.

Ionic liquid-assisted depolymerization

Ionic liquids are salts in which ions are poorly coordinated, resulting in a liquid state below 100°C. They possess interesting properties including low vapor pressures, chemical and thermal stability and the ability to dissolve a wide range of compounds, including lignin, and this in large amounts. According to Xu et al., one of the most important advantages of ionic liquids in lignin depolymerization is their ability to act as both an acidic catalyst and a solvent.¹⁴⁷ The depolymerization mechanism is similar to the mechanism proposed under acid-catalyzed conditions: the lignin undergoes proton-catalyzed breakage of β -O-4 linkages. Disadvantages are a very low lignin conversion, high costs, environmental hazards and recyclability of the ionic liquids. Because of these drawbacks, ionic-liquid assisted depolymerization has only minor prospects to become industrially feasible in the near future.

Supercritical fluid-assisted depolymerization

Also supercritical fluids can be used for lignin depolymerization since lignin is highly soluble in this kind of solvents. Depolymerization processes proceed with high selectivity. According to Pandey et al., the conversion of lignin in supercritical water occurs first by hydrolysis followed by dealkylation, resulting in low-molecular-weight fragments. Yields of monomeric phenols are much lower than expected, most likely due to repolymerization of monomers forming char.¹⁴⁸ Depolymerization of lignin can also be performed in supercritical alcohols like methanol or ethanol at high conversion rates. The dominant depolymerization mechanism is in these cases the solvolysis of ether linkages while the C-C linkages are mostly unaffected.¹⁴⁹ The presence of alcohols as solvent prevents repolymerization. By increasing the alcohol/lignin ratio, repolymerization can be inhibited and the formation of char can be significantly suppressed. Nevertheless, supercritical fluid-assisted depolymerization suffers from similar problems as ionic-liquid assisted depolymerization as there are high cost and demanding equipment.

Solvolytic depolymerization

Solvolytic depolymerization of lignin is a non-catalyzed process wherein water, organic solvents and mixtures thereof are used as reaction media.

According to Van den Bosch et al., temperature ranges between 250 and 450°C.¹⁴⁴ By lignin solvolysis, a wide variety of monomer products is generated. Main products are substituted and unsubstituted methoxyphenols. According to Schutyser et al., products with unsaturated and oxygenated side-chains are mainly obtained at temperatures below 300°C, while unsubstituted and alkyl-substituted compounds are mainly formed at higher temperatures.¹

Also the type of solvent has an effect on the type of products that are formed. In water or water/organic solvent mixtures, the yield of unsubstituted and alkyl-substituted compounds is higher, while solvolysis in hydrogen-donating solvents mainly generates methoxyphenols with alkyl side-chains.¹

Biggest advantage of solvolytic depolymerization is the simplicity, since no oxidants, reductants and acid/base additives are used. Disadvantage is the low monomer yield in most cases.

3. Biochemical depolymerization technologies

Process description

Within nature, lignin is efficiently degraded by basidiomyceteous white-rot fungi through multiple enzymes, illustrating the potential of biocatalysts for depolymerization of lignin. Biocatalysts can be much more selective than other catalysts and are able to distinguish between functional groups.¹⁵⁰ According to Gasser et al., application of enzymes in industrial processes is challenging since they are usually less stable than other catalysts, cannot be easily recycled and work only in a narrow temperature window.¹⁵⁰ Therefore, only a few papers on biological depolymerization are added to the BAFTA database.

Process conditions

Biocatalysts require mild reaction conditions (only a few enzymes are active at temperatures above 90°C) and cannot withstand organic solvents. Since lignin can be more easily dissolved in organic solvents, making it more available for catalysts, this is a big hurdle to take. Studies are ongoing on the immobilization of enzymes, increasing their stability and activity under various conditions.

Products

Since lignin itself is very complex and heterogeneous, composition of products obtained via application of microbes is complex as well. Within their review paper on lignin conversion, Ahmad and Pant describe

a process called biological funneling, where the upper metabolic pathway procures intermediates that pass through the lower metabolic pathway to yield aromatics.¹⁴⁵ In the upper metabolic pathway, lignin is converted into aromatic monomers such as catechol. In the lower metabolic pathway, ring opening and deoxygenation of obtained intermediates take place. Different types of enzymes are applied in upper and lower metabolic pathways.

CHAPTER 5: IP Landscape & FTO search for bio-aromatics derived from wood and lignin

Since the BAFTA project also intends to have an innovative character for wood biomass and lignin processing companies which will be responsible for the future production of the biobased building blocks, also an intensive IP study was performed. This was done by Aranca. The key aspects covered in the study are:

- technologies used for depolymerization of lignin/wood (Figure 3);
- different bio-aromatics that can be produced from lignin using the various depolymerization methods (Figure 4);
- applications of the obtained bio-aromatics in various industries.

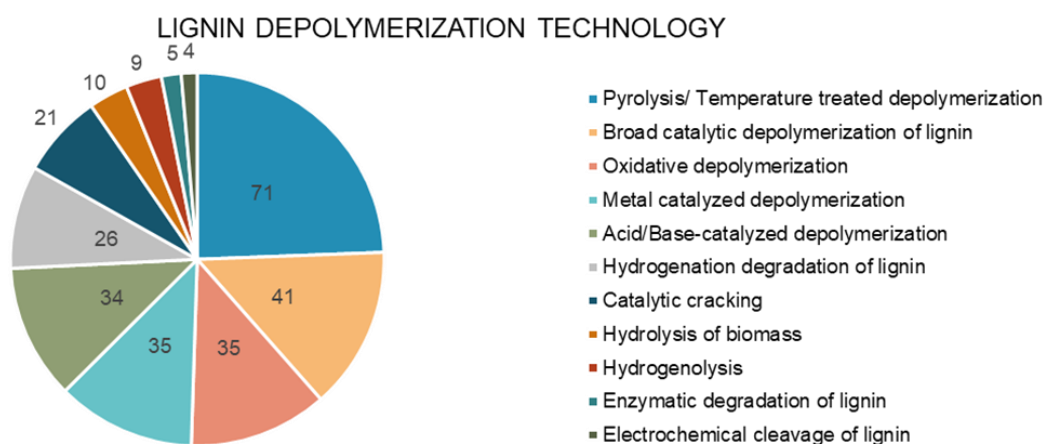


Figure 3: Overview of depolymerization technologies included in IP study

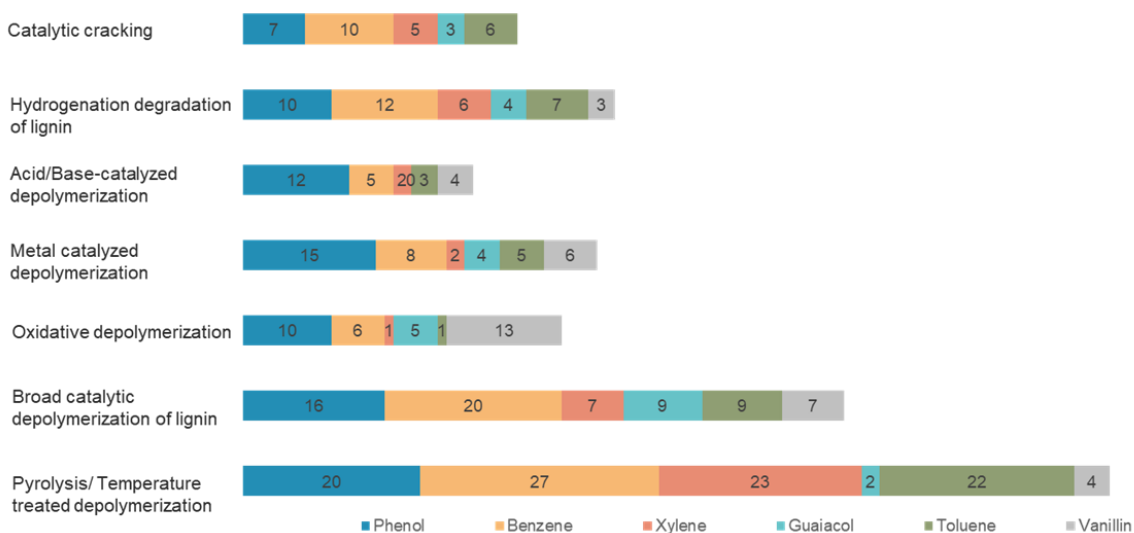


Figure 4: Identification of different bio-based aromatics produced by various depolymerization technologies

In total, 281 patent families were identified. The majority of patents/patent families focus on the lignin depolymerization process followed by the production of bio-aromatics. Major assignees are still working on problems of improving efficiency and yield. By mapping the patent landscape of conversion technologies, freedom-to-operate (FTO) for future investments and developments in the bio-aromatics industry in Flanders can be determined.

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