We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Base-Catalyzed Depolymerization of Lignin: History, Challenges and Perspectives

Björn Rößiger, Gerd Unkelbach and
Daniela Pufky-Heinrich

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.72964>

Abstract

Bio-based phenolic compounds available from lignin are promising candidates for industrial application, e.g., within polymer resins or as biogenic fuel substitutes. Among numerous conversion methods for the valorization of lignin, the base-catalyzed depolymerization (BCD) has considerable advantages with respect to other processes. By this method, lignin and lignin-containing biorefinery streams can be catalytically transferred to valuable, defined products with tailored specifications. Continuous process operation allows conversions at short residence times and, thus, enables its industrial implementation more easily due to economic reasons. This review reflects the development in the field of BCD on various types of lignin. A historical overview will be given and the principal application of the method is shown. Challenges for operations are addressed, mainly to the development of efficient and selective methods for product separation and purification of the alkylphenolic moieties and the reduction of char formation during the process. An outlook will be given by showing trends and perspectives, especially in the field of industrial applications. Here, hydrotreatment methods for refining BCD intermediates for fuel and platform chemical production are shown. Furthermore, the application of BCD for the conversion of woody biomass and black liquor is discussed.

Keywords: lignin, base-catalyzed depolymerization BCD, bio-based aromatic compounds, bio-based phenols, downstream processing, hydrogenolysis, hydrodeoxygenation

1. Introduction

Lignin is one of the major components in lignocellulosic biomass together with cellulose and hemicellulose and the world's only naturally occurring polymers, which is available as

a renewable resource in large quantities. Lignin is obtained as a major by-product during second-generation bio-ethanol production and also isolated as Kraft black liquor or lignosulfonates during pulp production. Also new lignocellulose bio-refinery processes for the production of chemicals or fuels will release an enormous amount of different kinds of lignin. Apart from its use in the form of wood, lignin is mainly used as energy source as a by-product of the paper and pulp industry. Every year, around 50 million tons of lignin are currently produced in this way worldwide. Conventionally, lignin is employed for the generation of heat and power in these industry processes [1]. Utilizations of lignin with regard to material application are only established to a limited extent. Increase in application depends solely on the availability of valuable chemicals synthesized from lignin that have a corresponding market value higher than their fuel value.

However, valorization of lignin is one of the most important challenges for the development of sustainable and cost-effective biorefinery processes based on lignocellulosic biomass. The alkylphenolic structure of the lignin molecule can be cleaved into low molecular weight compounds such as phenols, alkylphenols and phenol resins and replacing those obtained from fossil resources [2, 3]. The products are highly promising fuels or fuel additives [4, 5] or antifungal components [6] or can be used for the preparation of polyols and polyurethane resins [7]. Yet, the natural complexity and high stability of intramolecular bonds make lignin depolymerization a challenging task. Moreover, effective technologies for cleavage product separation from the reaction solutions are still subject of developments and have not been satisfactorily resolved. A prerequisite for industrial implementation are techno-economic feasible processes, which can be integrated into existing process chains. So far, low selectivity to defined products, subsequent separation and purification and char formation are the main hurdles for effective conversion of lignins. Among different methods, the so-called base-catalyzed depolymerization (BCD) is one option to transfer lignin and lignin-containing streams catalytically into valuable products even to those with narrow product specification. It can be operated in continuous process mode allowing conversions at short residence times (≤ 1 h) and low char formation. The latter is as phenomena, which might occur during hydrothermal conversion of lignin feedstock, and is an effect of concurrent repolymerization processes of lignin fragments during processing under the harsh reaction conditions needed [8].

This chapter comprehensively reviews the state-of-the-art applications and challenges for BCD processes of different kinds from solid lignin and lignin-containing feedstocks. It also points out future trends and perspectives in this field of research and development. Besides scientific approaches, methods and concepts for industrial implementation of this technology, e.g., in the pulp and paper industry or the chemical and process industry, are touched and discussed. In this context, patent applications on this subject are also mentioned, as well as processes and applications are discussed. In order to increase the technology readiness level of the BCD process and, thus, to develop an industry-relevant process, it is necessary to establish an overall approach regarding material and energy efficiency as well as to examine its technical and economic feasibility.

2. Methods on lignin depolymerization

Research in the field of lignin depolymerization is of strong interest. The number of scientific publications has developed exponentially in recent years and increased a hundredfold worldwide since 1980 starting with 2 to 1998 with 25 and until 2016 with 221 publications annually [9]. From this, it is evident that the viability of recovering of hydrocarbons and aromatics from lignins has been under intensive investigation over the past years. Literature and publications have been reviewed and extensively discussed in terms of the generation of valuable chemicals and fuels [1, 4, 5, 10–12] as well as derivatives for polymer resins [7]. Along with this and beyond, mechanistical aspects of chemical, biological and biotechnological depolymerization strategies are compared in detail and advantages and disadvantages as well as limits in their applications are presented [3, 13, 14]. The focus is primarily on the presentation of scientific work and innovations. Trends and new methods are partially presented in detail and summarized clearly. These include, above all, the current developments in transition-metal-catalyzed conversion of lignins for catalytic cracking, oxidation and/or hydrogenolysis for the utilization of lignin feed streams as fuels or fuel additives and bulk chemicals, respectively [2, 4, 13, 15].

Similar development can be overserved in the status on patent publications. Over the last decades, IP applications increased strongly in the last few years, whereas approximately 80% of patent applications have been made within the last 10 years [16]. The first application of BCD was published in 1983 by Stake Technology LTD as “process for depolymerization and extraction of lignin utilizing steam explosion technology” [17]. Technology applications might be found in the production of bioaromatic compounds for platform and fine chemicals [18, 19], as gasoline and biofuels [20, 21] or blending components [22].

2.1. Lignin structure

Lignin is a cross-linked amorphous three-dimensional copolymer synthesized from radical, random polymerization of the three primary phenylpropene units: coumaryl-, coniferyl-, and sinapyl-alcohols, joined by C—O—C (ether) and C—C bonds and collectively called monolignins (**Figure 1**). Structure and, thus, ratio of these three primary monomer units vary among different plants and species. In native lignin, the most abundant linkage is β -O-4 ether bond, which comprises around 45–60% of all linkages within lignin, whereas hardwood lignin contains roughly 1.5 times more compared to that of softwood. In total, approximately two third of linkages are ether bonds, while the others are C—C bonds [4, 11, 23]. The polyphenolic aromatic structure of lignin is ideally suited to obtain aromatic molecules, either as oligomeric derivatives or as low molecular weight monomeric compounds.

2.2. Strategies for lignin conversion

Chemical and enzymatic conversion strategies have been developed in recent years aiming to synthesize aromatic substructures or valorized chemicals from lignin. Lignin can be cleaved

Figure 1. Details of the lignin structure with its varying phenylpropene units connected by β -O-4 ether bond.

Figure 2. Summary of thermochemical processes for conversion of lignin; temperature applied vs. degree of functionalization within the product species.

by thermochemical processes that means by thermal treatment in the presence of various solvents, chemical additives or catalysts. Alternatively, there are approaches for enzymatic depolymerization using laccases or manganese peroxidases [24, 25]. A simplified summary of processes for chemical lignin conversion is given in **Figure 2**. Here, applied process temperatures are compared to the degree of functionalization within the product lignin species. Essential processes are pyrolysis, gasification, hydrogenolysis, chemical oxidation and hydrolysis. Depending on the process, the products of the depolymerization possess different proportions of gaseous (gas), liquid (oil) and/or solid (oligomers and/or char) products with

specific compositions. With pyrolysis, the thermal treatment at 300–600°C with exclusion of oxygen, mainly gaseous and volatile hydrocarbons, such as methane, ethane, acetone, methanol, acetaldehyde, phenol and carbon mono- and carbon dioxide, is formed. Gasification is a process in which lignin is converted at temperatures between 700 and 1000°C into a gas mixture of hydrogen, carbon monoxide, methane and carbon dioxide (syngas) [26]. The reductive cleavage with hydrogen (hydrogenolysis) leads to a mixture of differently substituted phenols and benzenes, whereas products of oxidative cleavage are mostly phenolic aldehydes such as vanillin and syringyl alcohol [11]. With hydrolysis, the ether bonds in the lignin are cleaved by a homogeneous or heterogeneously catalyzed aqueous reaction. The hydrolytic cleavage can be further categorized according to different chemicals applied in the depolymerization process, namely base-catalyzed, acid-catalyzed and metal-catalyzed or with the aid of ionic liquids or supercritical fluids. Wang et al. summarized recent scientific developments with regard to this classification [14]. Depolymerization methods have also been reviewed according to the product specification, which is either gaseous as methane, carbon dioxide and formaldehyde or liquid as a so-called bio-oil [27]. This view is very product-driven and above all illustrates the scope of application of lignin-derived products. From the point of view of chemists and process engineers, classification is also carried out according to the mode of chemical conversion. Homogeneous and heterogeneous catalytic conversions are in this case considered separately and thus condition the process design and process implementation [5, 12].

3. Base-catalyzed depolymerization of lignin

3.1. Nature of base-catalyzed depolymerization of lignin

All degradation strategies have the objective of reducing the complexities of the natural lignin molecule, lowering its molecular weight and, moreover, increasing the chemical reactivity of the degradation products. Three fractions are formed: liquid oil; oligomers, often called tar fraction; and higher polymeric lignin species called char. Side products are formic acid, acetic acid, methanol and carbon dioxide. This is compared to degradation processes such as pyrolysis and hydropyrolysis, which lead to a mixture of oligomer and polymer oxyaromatic fractions. The latter is caused by the initiation of radical formation inside the lignin molecule during the cleavage of weak phenolic bonds. Subsequently, recombination of radical moieties may lead to the formation of new kinds of carbon-carbon bonds and ultimately to oligomers and higher condensed structures named as char. The BCD of lignin is carried out in dilute alkaline solution at temperatures between 250 and 350°C, high pressures (150–300 bar) and short residence times (5–15 min), preferably performed in a continuous flow tube reactor to ensure short residence times and, thus, to avoid repolymerization.

In principle, lignin is cleaved into a mixture of aliphatic degradation products (methanol, formic acid and acetic acid), phenolic mono- (e.g., guaiacol, syringol and catechol), di- and oligomers and carbon dioxide. This reaction mode is simplified in **Figure 3**.

Figure 3. Reaction scheme for cleavage via base-catalyzed depolymerization (BCD) at β -O-4 ether bonds (red) with structures of lignin, BCD-oil (phenolic mono- and dimers), BCD-oligomers (phenolic oligomers) and BCD-by-products (organic acids, alcohols and gases).

Mechanism of bond-breaking and product formation: Lignin is solved in alkaline water, whereas the alkaline or earth alkaline metal ions polarize the ether bond. At reaction conditions, bond-breaking occurs mainly at the β -O-4 bond (aryl-glyceryl- β -aryl ether bond) and the 4-O-5 bond (diaryl ether bond) as aryl-alkyl-ether bonds are the weakest bonds in lignin. According to the structure of the lignin molecule, up to 25% of monomer units, i.e., phenol, guaiacol, syringol and catechol derivatives, are formed. The ideal process would be a reaction affording high yields in monomers and, thus, a nearly entire cleavage of all aryl-ether bonds within the lignin molecule [28].

A detailed description and analytical characterization of the monomeric aromatic compounds is given in [28–31]. In addition to these monomers, a large proportion of dimeric and oligomeric structures are obtained having the following types of bonds: 5-5 (biphenyl bond), β -5 (phenylcoumaran), β - β (THF or resinol type) and β -1 (1, 2-diarylpropane). These compounds accumulate in the liquid product (BCD-oil) depending on the processing method for separation. The BCD-oligomer fraction contains oligomeric polyphenols, higher condensed structures and unreacted lignin. Short-chain acids formed during the reaction neutralize the base and can hinder the hydrolysis process. At worst, the pH in the reactor drops to such an extent that dissolved phenolates precipitate in the reactor, which can lead to clogging and blockages of the reactor. For this reason, the pH value, due to a sufficiently high base concentration, must be at least pH 12 at all times [32].

Demethoxylation and demethylation reaction also occur at more harsh process parameters resulting in the formation of catechol-type molecules with simultaneous formation of methanol, formic acid and acetic acid. A shift in the yield to catechols with simultaneous decrease in syringol concentration was clearly demonstrated by BCD of beech wood organosolv lignin

and kraft lignin operating above 300°C. Here, the formation of catechol-type monomers by BCD, in the absence of a H₂ donor, mainly depends on retention in the reactor and the process temperature [28]. Investigations on hardwood organosolv lignin showed demethoxylation processes starting at 280°C by decreasing syringol concentration in the monomeric product phase [33]. Kinetic studies on lignin model compounds mimicking the alkyl-aryl or aryl-aryl-ether linkages have shown that BCD is a rapid reaction that occurs within minutes under appropriate conditions [2, 32].

In general, the presence of alkali and earth alkali in base media modifies the reaction routes, facilitates bond-breakings and in some cases enhances the formation of formic or acetic acid during the depolymerization process. Moreover and as already reported earlier, base catalysts are required in water to solubilize the lignin feedstock, to avoid coke formation and to increase liquid product yield. Condensation reaction is conspicuously suppressed during BCD processes compared to process in acid or neutral media [34].

3.2. State of the art and overview

Bond-breaking and recombination are strongly defined by process conditions, namely temperature, pressure, residence time and base concentration along with the type of feedstock used. Equally important is the chemical nature of the base. **Table 1** shows selected examples of BCD strategies and compares striking process parameters. In this case, only reactions in liquid homogeneous phase without the use of additional catalyst systems or other reaction agents were considered.

3.2.1. Lignin nature

The catalytic reagents are cheap and commercially available bases such as LiOH, NaOH and KOH. Its nature is important for the oil yield and product composition. Usually, stronger base gives higher conversion since the polarization of the base governs the kinetics and the mechanism of the depolymerization reaction. Highest BCD-oil yield could be observed with NaOH. Utilizing Ca(OH)₂ results in low BCD-oil formation when processing olive tree pruning lignin at 300°C [34]. Another example also describes that using strong bases (KOH and NaOH) converts more of the lignin to low molecular weight products than weak bases (LiOH, Ca(OH)₂ and Na₂CO₃). Here, maximum conversion was achieved at a NaOH/lignin ratio of 1.5–2. Higher ratios increased the conversion rate but not the conversion degree to lower molecular weights and higher BCD-oil yields. The optimum was given with 8 wt.% of insoluble material at a reaction time of 1 h at 330°C in batch microreactor system using up to 10 wt.% of lignin in solution. Further, depolymerization is more efficient and less dependent on temperature at higher base concentration [35]. This observation was also reported by Miller et al. and Roberts et al. who had found less insoluble products (unconverted lignin) with increasing NaOH/lignin ratios [32, 33]. In general, base concentration has to be sufficient in order to fully polarize and deprotonate the phenolic and catecholic species to alcoholates. This must be taken into account, in particular, in that the base concentration decrease during the cleavage process, as new hydroxyl groups, reactive organic acids and carbon dioxide are formed.

Feedstock	Base catalyst	Reaction parameters		Products and composition	Reference
		Reaction conditions	Reaction system		
Alcell/indulin lignin	10 wt.% lignin in MeOH or EtOH/CsOH, NaOH, KOH, LiOH Ca(OH) ₂ or Na ₂ CO ₃ - sol.	290°C, 60 min	Batchwise	Ether-soluble products ≤93 wt.%	[32]
Beech wood organosolv lignin and lignoboost kraft lignin	5 wt.% lignin in 1–5 wt.% NaOH-sol.	250–340°C, 250 bar; 5, 10, 15 min	Continuous mode, plug-flow reactor	Oil content ≤23 wt.%	[28, 39]
Organosolv lignin	2.5–10 wt.%, 2.5 wt.% NaOH-sol.	240–340°C, 250–315 bar, retention time 2–15 min	Continuous mode, plug-flow reactor	~ 15 wt.% oligomers, ~ 22 wt.% oil	[33]
Steam explosion hemp-lignin	5 wt.-% lignin in NaOH-sol.	300–330°C, 90–130 bar	Batchwise	Up to 11 wt.% monomer species	[29]
Softwood indulin lignin	10 wt.% lignin in 5 wt.% NaOH sol.	270–315°C, LHSV 1.4–4 h ⁻¹	Continuous mode, plug-flow reactor	Small organic compounds ≤19 wt. %, solid products ≤70 wt.%	[37]
Organosolv lignin from olive tree pruning	4 wt.% lignin in NaOH, KOH, LiOH or K ₂ CO ₃ – sol.	300 °C, 900 bar	Batchwise	Oil (monomers and dimers), yield 5–20 wt.%	[34]
Olive tree pruning organosolv lignin	5 wt.% lignin, 4 wt.% NaOH-sol.	300 °C, 90 bar, 80 min	Batchwise	Oil components ≤18.5 wt.%	[36]
Lignin-rich residue from corn stover	10 wt.% lignin, 2–4 wt. % NaOH sol.	270–300°C	Batchwise	Aqueous soluble fraction ≤78 wt.%	[31]
Gray ironbark organosolv lignin	5 wt.% lignin, 4 wt.% NaOH sol.	300 °C, 40 min	Batchwise, microreactor	Oil components ≤21.9 wt.%, solid products ≤58.3 wt.%	[6]
Beech wood organosolv lignin and kraft lignin	2.5–10 wt.% lignin in 2.5–7.5 wt.% NaOH-sol.	300–340°C, 250 bar; retention time 450–900 s	Continuous mode, plug-flow reactor	Oil content ≤14.5 wt.%	[8, 38]
Lignin-rich residue from corn stover	10 wt.% lignin, 1–2 wt. % NaOH sol.	60–240°C, 0.7–20 bar	Batchwise	Aromatic acids	[35]

Table 1. Selected examples and comparison of BCD of different kinds of lignin at various process conditions.

3.2.2. Nature of the catalyst

Similarly, it can be said that, besides, the base concentration temperature is the most important factor and has the strongest influence on the yield of oil and solid fractions. By cleaving organosolv lignin and sulfur-containing kraft lignin, it was shown that higher process intensity

(temperature, pressure and residence time) results in higher depolymerization degree and, thus, in growing formation of monomeric and dimeric phenolic products and also of gaseous and liquid degradation products. Temperature influences not only the yield but also the molecular composition caused by the already mentioned successive reactions such as decarboxylation and demethoxylation at the substituent and side chains of the aromatic ring in the lignin molecule [8, 38].

Usually, the ether hydrolysis starts at 250°C. Ideal process conditions are described between 300 and 340°C in order to achieve complete cleavage of the ether bonds and to obtain a high yield of liquid products (see **Table 1**). Investigation on BCD at lower temperatures down to 60°C showed a poor yield on liquid products. On the other hand, at very mild reaction temperatures of up to 140°C, the exclusive formation of coumaric and ferulic acid can be observed [35]. Low yields are not surprising due to the manufacturing process of the lignin. Nearly all lignin preparation methods are thermochemical processes using temperatures between 150 and 180°C (e.g., kraft-, organosolv- and steam-explosion lignin).

3.2.3. Influence of the processing conditions

The composition of softwood and hardwood lignin is varying in the relative abundance of coumaryl, coniferyl and sinapyl alcohol units. Coniferyl alcohols constitute approximately 90% of softwood lignin, whereas roughly equal proportions of coniferyl alcohol and sinapyl alcohol appear in hardwood lignin [2]. These structural differences significantly influence the product composition. This was clearly showed in the comparison of BCD of hardwood organosolv lignin with softwood kraft lignin. Syringol and dimethoxyphenols are found almost exclusively in the BCD-oil of organosolv lignin with a significant amount in the monomer phase [8, 28, 30]. Other studies focused on the investigation of one type of wood but with different pretreatment methods applied. Erdocia et al. investigated the BCD of lignin from olive tree pruning fractioned by different organosolv processes, namely acetosolv, formosolv and acetosolv/formosolv. It could be summed up that low molecular weight lignin leads to more monomeric phenolic compounds, whereas the amount of obtained residual lignin is independent of the lignin nature [36]. The pretreatment method of the lignin stream has a significant influence on the product yields and nature since successability to BCD is strongly influenced by lignin structure and the amount of impurities, like carbohydrates, in the feedstock. Different mechanically refined substrates and acid-pretreated lignin-rich feedstock have been examined by Katahira et al. and the product dependence on the pretreatment has been demonstrated [31].

3.3. Challenges

3.3.1. Repolymerization and char formation

It is also proposed that in early stage of the hydrothermal treatment, lignin was decomposed to water-soluble fragments, and with the increase of the reaction time, the soluble products were transformed to insoluble products by recondensation reactions. Investigations on model compounds confirmed the theory that the two processes of lignin depolymerization and

repolymerization are concurrent. The latter often leads to products that are more resilient than the initial lignin due to C—C bond formation [40, 41]. In the case of lignoboost kraft lignin processed at 350°C and 250 bar, high molecular weight fractions were found consisting of repolymerized macromolecules with new structural networks based on guaiacol, disubstituted aromatic ethers and polyaromatic hydrocarbon structures bound tightly together [42].

In order to overcome this phenomenon, the reaction parameters that determine the amount of repolymerization need to be optimized and the amount of lignin in the mixture should be carefully balanced [8, 12]. In addition, there is a need to scavenge and deactivate the reactive species possessing phenol, carbonyl or alkene functionalities. Boric acid acts as an excellent protecting or capping agent by forming esters with phenolic hydroxyl groups and, thus, reducing concurrent reaction of polymerization. The highest oil yield of 52 wt.% was found at an NaOH/boric acid ratio of 0.75 at 300°C and boric acid/lignin weight ratio of 2. Oil yield could be doubled relative to the standard NaOH-catalyzed process [33]. Similar results have been found utilizing phenol as capping agent. Interestingly, this method was proven to favor phenolic compound production (cresol, catechol and ferulic acid) and, at the same time, to avoid repolymerization [43].

3.3.2. Separation, purification and analytical characterization strategies

The assessment of process efficiency and selectivity requires the application of separation and purification methods for sample preparation and accurate analytical protocols for the specification and characterization of main and by-products. The methods described in literature are just as multivarious as depolymerization strategies. Kozliak et al. recently reviewed the efficiency, selectivity and product analysis of thermal liquefaction processes of lignin to aromatics [41]. Overall objectives are the detection and quantification of specific structural changes altered by depolymerization reaction, the separation and identification of individual phenolic compounds/fractions and attempts to close the mass balance.

Solid product fraction: Conventionally, downstream processing of the reaction outlet starts by precipitating the solid BCD fraction by adding a strong acid, e.g., sulfuric or hydrochloric acid. If possible, this quench must be carried out immediately after BCD in order to prevent further reaction and repolymerization of the phenolic compounds. The product slurry is subsequently treaded to separate water-soluble and water-insoluble products by centrifugation and/or filtration. Heating the precipitated suspension to 70°C for 15 min can significantly improve the filterability of the suspension [29]. This strategy is especially recommended for gravimetric determination of the BCD-oligomer fraction, since minor yield losses, water and ash contents compared to centrifugation. Analytical methods for structure identification include GPC, FT-IR, TGA, ¹H-NMR, ¹³C-NMR and elemental analysis. Furthermore, an organic solvent solubilization is often used for further fractionation of the solid fraction. Toledano et al. used THF in order to separate lignin-derived oligomers (THF-soluble fraction) and coke (THF-insoluble fraction) [34].

Liquid product fraction: Strategies for the separation of value-added monomers from the BCD cleavage have been done by Vigneault et al. utilizing a steam-exploded aspen lignin. In addition to the described downstream strategy, a concept for the isolation of 12 monomeric

lignin derivatives was shown. The strategy combines liquid-liquid extraction with subsequent vacuum distillation of monomers and liquid chromatography and crystallization for purification of the products like catechol, phenol, guaiacol derivatives, syringol derivatives and vanillin [44]. Unkelbach et al. evaluated organic solvents of different polarity (DCM, EtOAc, MIBK and toluene) for the extraction of different phenols from acidified/filtered BCD reactor water (pH value = 3). The extracts were analyzed gravimetrically and by GC- and LC-MS. The highest amount of oil was achieved with MIBK (28 wt.% of lignin). Extraction with EtOAc, DCM and toluene led to lower oil amounts (23, 12 and 9 wt.%) [39]. The results of Greminger et al. from measurements of equilibrium distribution coefficients for phenol, dihydroxybenzenes and trihydroxybenzenes also lead strongly toward the use of MIBK as a preferred solvent, especially for polyhydric phenols [45].

Extraction methods are particularly suitable for identification and quantification of individual phenolic compounds by gas chromatography and gravimetric determination of selectivities referring to the used organic solvent. Additional characterization methods of the phenolic fraction are thin-layer chromatography, IR, ^1H - and ^{13}C -NMR. Total carbon (TC) measurement of BCD reactor water is recommended for mass balance, including all inorganic and organic compounds.

Gaseous product fraction: Joffres et al. characterized liquid, solid and gaseous products after batch catalytic ($\text{NiMo}/\text{Ag}_2\text{O}_3$) hydroconversion of a wheat straw soda lignin (Protobind 1000) for 5 h at 350°C , 8 MPa in tetralin solvent. Gaseous products were carbon dioxide (major gas), carbon monoxide, methane and light hydrocarbons (ethylene, ethane and propane), identified by GC-TCD/MS [12]. Long et al. analyzed gaseous products after batch depolymerization of pine lignin ($220\text{--}280^\circ\text{C}$, 15–60 min) in MgO/THF solvent but did not take them into mass balance account, as the total amount was less than 1% of raw lignin [46]. BCD of commercial kraft lignin (indulin AT) was performed at $270\text{--}315^\circ\text{C}$, 130 bar and 15–45 min residence time (flow reactor) by Beauchet et al. quantifying gases (13,2–25,5%) by difference [37].

Generally, the chemical composition of the BCD reaction product mixture depends on the type and concentration of the lignin feedstock, the solvent and catalyst and the reaction conditions (temperature, pressure and retention time). A wide spectrum of gaseous (mainly CO_2), liquid (monomeric/dimeric oxyaromatics and low MW compounds, e.g., formic acid, acetic acid and methanol) and solid products (oligomeric oxyaromatics) formed during BCD degradation. Commonly used and promising separation, purification and analytical strategies are summarized at **Figure 4**.

3.3.3. Increasing the technology readiness level for industrial implementation

Industrial implementation of the processes requires fast processing in continuous operated reactors and plant equipment that can be implemented in existing infrastructures. Here, an economically sensible mode of operation is a prerequisite for the application of BCD in the process industry. A full commercial application where the technology is proven in operational environment and available for customers has not been launched so far (equal to technology readiness level TRL 9) [47]. Research activities in the field of BCD of lignin mostly range from applied research activities to small-scale prototypes in laboratory environment (TRL 3–4).

Figure 4. Strategies of separation, purification and analytical characterization of BCD cleavage products (W, water; L, lignin; B, base solvent; ML, modified lignin; C, coke; MDO, phenolic mono-, di-, and oligomers; WSO, water-soluble organics; S, salts).

Large-scale prototypes for plant equipment tested in intended industrially relevant environment close to expected performance (TRL 5-6) have been reported only by Rößiger et al. so far [8]. This includes not only the cleavage but also the corresponding downstream processing for the isolation and purification of the two product fractions BCD-oil and BCD-oligomers.

Commonly used batch reactors have inherent disadvantages including the alternation of heating and cooling, pressurization and depressurization, with inevitable energy losses [41]. Moreover, it can be pointed out in literature that char formation caused by repolymerization can be minimized by continuous operation of the BCD process due to a precise setting of the reaction parameter temperature and residence time. A customized engineering design of the reactor results in precise heating and cooling rates, residence time distribution and adjusted material design. Dedicated reactor systems have been described at laboratory and technical lab scale [18, 28, 33, 48] and also at a more upscale and direct approach [37] and in pilot scale [8]. The comparisons of the individual technologies are shown in **Table 2**.

Feedstock	BCD process	Reaction and reactor parameters		Reference
		Reaction conditions	Reaction system	
Hardwood organosolv lignin	In NaOH/aqueous solution with and without boric acid as capping agent, homogeneous phase	240–340°C, 250–315 bar, retention time 2–15 min	Plug-flow continuous mode, lab scale***	[33]
Beech wood organosolv lignin and kraft lignin	In NaOH/aqueous solution with and without formic acid as hydrogen donor, homogeneous phase	300–340°C, 250 bar, retention time 5, 10, 15 min	Plug-flow, continuous reactors, 0.25 L reactor volume**	[28]
Softwood indulin lignin	In NaOH/aqueous solution, homogeneous phase	270–315°C, LHSV 1.4–4 h ⁻¹	Plug-flow, continuous reactors, 1.0 L reactor volume	[37]
Lignoboost kraft lignin	In NaOH/aqueous solution with ZrO ₂ catalyst with and without phenol as accepting agent, heterogeneous phase	350 °C, 250 bar, feed rate 1 kg/h	Fixed-bed continuous batch reactor, reactor volume 0.5 L	[48]
Alkali lignin and ligno-sulfonic acid	In base/water system and additional reagents, e.g., oxygen, peroxides and copper nitrate, homogeneous phase	200–380°C, 150–350 bar, residence times to 90 s	Plug-flow continuous reactors sequentially connected in series, total volume 9.8 ml**	[18]
Beech wood organosolv lignin and lignoboost kraft lignin	In NaOH/aqueous solution, homogeneous phase	250–340°C, 250 bar, retention time 450–900 s	Plug-flow, continuous reactors, 2.2 L reactor volume	[8]

*Size and flow rate not depicted.
 **Quenching of the lignin solution with hot aqueous solution.

Table 2. Compilation of publications on BCD in continuous operation.

Heterogeneous catalysis has been performed in a continuous batch reactor applying a fixed bed of ZrO₂ catalyst [48]. For homogeneous base/aqueous feed streams, plug-flow reactor models are used. The heat input is predominantly realized via electrical preheaters and electrically operated heating jackets, whereby the lignin solution might be fed directly into the reactor. **Figure 5** shows the flow sheet of a pilot plant (feed rate up to 20 kg/h) for BCD cleavage operating with lignin feed streams up to 10 wt.% and subsequent isolation of the liquid-base product solution [8]. Cofeeding of the lignin/base solution to a water stream heated to operational temperature is an alternative approach that has been described several times in technical lab scale design [18, 28, 33]. Here, the two streams, water and lignin/base solution, are mixed right before entering the reactor. This procedure allows a precise heating of the lignin solution to the reaction temperature, thus, leading to a more exact and precise temperature control and also avoiding overheating in the system caused by preheating the lignin solution. As a consequence, the enhanced formation of higher molecular weight lignin fragments with a broad molar mass distribution is reduced, but the whole reaction solution is diluted due to the necessary secondary water stream. However, downstream-processing might be more consuming and expensive.

Figure 5. Schematic flow sheet of the plant for BCD depolymerization in pilot scale [8].

4. Trends and perspectives

The following chapter deals with developments beyond the original BCD in a homogeneous liquid phase. Innovative designs and processes include novel catalyst systems, subsequent and coupled reaction modes and the use of innovative reaction media. The depolymerization of lignocellulose-containing feedstocks by BCD has already been investigated and will also be discussed here exemplarily.

4.1. Solid-phase catalysts for improved lignin degradation

An efficient and economical catalytic system using the available industrial solid-phase catalyst MgO has been described by Long et al. [46]. Conversion rates in water system operating at 250°C show satisfactory results in conversion of lignin. Due to its excellent dissolution capabilities and the promotion effect for the catalyst organic solvent, in particular THF, it is found to be an efficient reaction media and leads to a significant increase in conversion rate. It was also shown that zeolite catalysts (NaX, NaY and NaP) lead to improved yield on monomeric products compared to other catalysts like MgO or CaO. A maximum of 51 wt.% of low molecular weight products was achieved in an ethanol/water medium at 250°C [23]. Layered double hydroxides (LDH) as recyclable, heterogeneous catalysts have been introduced recently for BCD of lignin. Such solid-base catalysts avoid the cost of liquid phase, nonrecyclable base and downstream processing steps like neutralization. LDH are prepared from Al and Mg salts and are stable in water and organic solvents at relatively high working temperature [49, 50].

4.2. Upgrading of BCD products by catalytic refinement

Lignin-derived fractions cannot be utilized directly as fuels or fuel additives due to their high oxygen content, acidity, instability, high viscosity and complexity of constituent compounds. It should be mentioned at this point that O/C ratio and H/C ratio of fossil species are 0 to 0.03 and from 1.6 to 2.1, respectively. In contrast, the O/C and H/C ratios of the BCD bio-oils range from 0.6 to 0.7 and from 1.0 to 1.35, respectively. Upgrading the cleavage products should therefore target oxygen removal, carbon preservation and hydrogenation of unsaturated carbon bonds. Thus, catalytic upgrading processes to convert the alkoxyphenol species are required for further chemical transformation to the improved and enhanced products. Procedures typically focus on further reduction in the oxygen content via hydrodeoxygenation (HDO) and/or further cleavage with larger oligomeric fragments of the oil, as so-called hydrocracking (HC). Solvolysis of lignin-utilizing reductive agents is summarized as hydrogenolysis (HGL) [3, 40, 51].

Hydrogenolysis of lignin: HGL has been investigated for decades and combines C—O bond-breaking with simultaneous hydrogenation at C and O moieties. Hydrogen-donating solvents such as tetralin, formate or anthracene species have been successfully tested. Also alcohols have been widely used for *in situ* generation of hydrogen [5, 52]. These are highly attractive methods, especially considering that methanol or ethanol can be potentially derived from lignocellulose or other renewable resources. Hydrogen transfer from methanol over basic copper catalyst under supercritical or milder conditions reveals the formation of aromatic and aliphatic alcohols. The role of the multifunctional catalyst is to promote reforming of the methanol solvent to CO and H₂ that serve thereby as a “liquid syngas” and to catalyze diverse hydrogenolysis and hydrogenation processes. The latter consumes the produced hydrogen equivalents [13]. Besides, hydrotreating and hydrothermal treatment of alkaline lignin in methanol over Ru/Al₂O₃ have been found to improve product yield and selectivity and reduce char formation at lower working temperatures and pressures [53].

Another approach is introducing hydrogen H₂ directly into the reaction media within pressurized systems. Activation of H₂ is mandatory and realized by using various heterogeneous catalyst systems. Supported Ni (on Al₂O₃) or Ru (on carbon) materials have been used for example to break down lignin into monomeric units by introducing hydrogen at pressure up to 70 bar [5, 54]. To mention at this point is also the use of ionic liquids as a solvent and in parallel as an acid catalyst for improved product refinement. The amount of total hydroxyl groups could be increased in the final cleavage product using 1-butyl-3-methylimidazolium chloride (BMIM Cl) in the presence of H₂, compared to the original used soda lignin. As a result, lignin antioxidant activity was enhanced [55].

In a one pot system, lignin can also be directly transferred to some aliphatic hydrocarbons in the so-called lignin to liquid process (LTL process). Kleinert et al. have introduced this method for fully liquefying lignin using formic acid, ethanol and i-propanol [52].

Hydrodeoxygenation of BCD intermediates: Catalytic hydrodeoxygenations are mostly appended to the BCD process. They are used to produce aromatic hydrocarbons and

alkyl-cycloalkanes with low oxygen content and high stability. Within these kinds of processes, C—O bond-breaking occurs, and C—O, C—C and C—H bonds as well as the aromatic rings will be saturated. While oxygen is partially and selectively removed, acidity of the intermediates is lowered resulting also in an inhibition of repolymerization. Hereby, mixtures of aromatics and alkanes with narrower product distribution are generated, which contain oxygen-poor, low molecular weight molecules, giving access to biofuels and bulk chemicals [3].

Consequently, a significant part of the developments is found in patent applications. Processes combining several internal steps are also published. Mild BCD at up to 240°C is followed by selective hydrocracking with superacid catalyst. The resulting oxygen-containing depolymerized lignin of alkylphenols will further be catalytically etherficated with methanol or ethanol leading to reformatted partially oxygenated gasoline [20, 22]. Also the developments for liquid biofuel synthesis by subsequent BCD and HDO processes to C7-C11 alkylaromatic compounds and paraffins should be mentioned [21, 56]. Cobalt and molybdenum catalysts [21, 56] or iron oxides [57] in the presence of H₂ are utilized. Subsequent catalytic oxidation with peroxides of BCD intermediates is rising the production of useful platform and fine chemicals [18].

4.3. Utilizing black liquor and lignocellulose feedstock

Depolymerization of black liquor without isolation of lignin might be advantageous over solid lignin processing since the stage of precipitation could be bypassed, reducing the costs of the whole process chain. As kraft black liquor presents an alkali medium, BCD depolymerization of lignin can be carried out similarly to isolated lignin in order to obtain small phenolic compounds. A direct comparison for the conversion of solid soda lignin and soda black liquor revealed a higher conversion degree for black liquor. Yields of BCD-oil and BCD-oligomers were significantly higher, with less formation of char [36]. The application of catalytically active reagents, such as phenols or hydrogen peroxide, also markedly increases the amount of small phenolic compounds and prevents repolymerization to undesirable products (residual lignin and coke) [58].

Current developments also include the direct transformation of woody biomass and other lignocellulosic feedstock for the production of aromatic building blocks. An especially interesting concept is the process of transferring hydrogen equivalents from cellulose fraction into lignin. Copper-doped basic heterogeneous catalysts are well suited for the conversion of both lignin and cellulose-derived feedstocks into alcoholic species where humin formation is suppressed [13].

Furthermore and beyond the previous examples, we want to mention a remarkable development for reductive lignocellulosic fractionation at this point. The innovative catalytic lignin's first LF process aims at the direct and selective conversion of lignin directly from wood pellets, allowing a high conversion into monomeric and some dimeric alkyl phenols next to small oligomers. In the presence of a Ru on carbon catalyst (Ru/C) in methanol under H₂ atmosphere at elevated temperature, lignocellulose sawdust is efficiently delignified through simultaneous solvolysis and catalytic hydrogenolysis, resulting in a carbohydrate pulp and a lignin oil [59, 60].

5. Conclusion and closing remarks

Current research and development activities address the optimization of product specifications from BCD cleavage with regard to low molecular weight alkylphenols and alkylphenols possessing narrow molecular weight distribution. Reactive additives, such as phenols or organic alcohols, are used to suppress repolymerization and condensation of product intermediates and, thus, to avoid char formation. However, complex mixtures consisting of molecules with relatively high oxygen content restricts its implementation in the usual process chains of the chemical and process industries. Therefore, concurrent or subsequent hydrodeoxygenation or hydrolysis of BCD-oils or BCD-oligomers is applied for further refinement and gives rise to the use as bulk chemicals or fuels. Significant effort has been made in recent years to advance developments in this area. But yet, industrial implementation has not taken place. Therefore, one has to ask at this point whether the utilization of lignin as low-priced products in the form of platform chemicals appears to be economical. Material use is usually in competition with its energetic use in the form of black liquor or other biorefinery lignin feedstocks. The production of fine chemicals and specificities by means of the BCD process might offer the possibility to provide even high-priced products made of lignin. In particular, functional monomeric derivatives, such as vanillin, syringaldehyde or apocynin, are interesting candidates. Even a cascade of uses, for example, low molecular weight aromatics in the field of fine and platform chemicals and medium and high molecular weight fractions as polymer additives, is worth mentioning here.

In order to increase the technology readiness level of the BCD process and, thus, to develop an industry-relevant process, it is necessary to establish an overall approach regarding material and energy efficiency as well as to examine its technical and economic feasibility. Still one of the biggest limitations for its commercial application is the obtainment of complicated product mixtures. The low selectivity to products and subsequent required separation and purification are the main hurdles for lignin cleavage processes. Therefore, new innovative approaches and technologies especially for downstream processing, like membrane techniques, have to be considered.

Author details

Björn Rößiger, Gerd Unkelbach and Daniela Pufky-Heinrich*

*Address all correspondence to: daniela.pufky-heinrich@igb.fraunhofer.de

Fraunhofer Center for Chemical-Biotechnological Processes (CBP), Leuna, Germany

References

- [1] Kamm B, Schmidt M, Hirth T, Schulz M. Lignocellulose-based chemical products and product family trees. In: *Biorefineries—Industrial Processes and Products: Status Quo and Future Directions*. Weinheim: Wiley; 2006. pp. 67-84

- [2] Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*. 2010;**110**(6):3552-3599. DOI: 10.1021/cr900354u
- [3] Graglia M, Kanna N, Esposito D. Lignin refinery: Towards the preparation of renewable aromatic building blocks. *ChemBioEng Reviews*. 2015;**2**:377-392. DOI: 10.1002/cben.201500019
- [4] Li C, Zhao X, Wang A, Huber GW, Zhang T. Catalytic transformation of lignin for the production of chemicals and fuels. *Chemical Reviews*. 2015;**115**(21):11559-11624. DOI: 10.1021/acs.chemrev.5b00155
- [5] Xu C, Arancon RAD, Labidi J, Luque R. Lignin depolymerisation strategies: Towards valuable chemicals and fuels. *Chemical Society Reviews*. 2014;**43**:7485-7500. DOI: 10.1039/C4CS00235K
- [6] Dos Santos PSB, Erdocia X, Gatto DA, Labidi J. Bio-oil from base-catalyzed depolymerization of organosolv lignin as an antifungal agent for wood. *Wood Science and Technology*. 2016;**50**(3):599-615
- [7] Mahmood N, Yuan Z, Schmidt J, Xu C. Hydrolytic liquefaction of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam. *Green Chemistry*. 2016;**18**:2385-2398. DOI: 10.1039/C5GC02876K
- [8] Rößiger B, Röver R, Unkelbach G, Pufky-Heinrich D. Production of bio-phenols for industrial application: Scale-up of the base-catalyzed depolymerization of lignin. *Green and Sustainable Chemistry*. 2017;**7**(3):193-202. DOI: 10.4236/gsc.2017.73015
- [9] Web of Knowledge [Internet]. 2017. Available from: <https://www.wcs.webofknowledge.com/RA/analyze.do> [Accessed: 2017-11-01]
- [10] Abdullah B, Muhammad SAFAS, Mahmood NAN. Production of biofuel via hydrogenation of lignin from biomass. In: *New Advances in Hydrogenation Processes—Fundamentals and Applications*. Rijeka, Croatia: InTech; 2017. DOI: 10.5772/66108
- [11] Azadi P, Inderwildi OR, Farnood R, King DA. Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renewable and Sustainable Energy Reviews*. 2013;**21**:506-523. DOI: 10.1016/j.rser.2012.12.022
- [12] Joffres B, Laurenti D, Charon N, Daudin A, Quignard A, Geantet C. Thermochemical conversion of lignin for fuels and chemicals: A review. *Oil & Gas Science and Technology*. 2013;**68**(4):753-763. DOI: 10.2516/ogst/2013132
- [13] Deuss PJ, Barta K. From models to lignin: Transition metal catalysis for selective bond cleavage reactions. *Coordination Chemistry Review*. 2016;**306**(2):510-532. DOI: 10.1016/j.ccr.2015.02.004
- [14] Wang H, Tucker M, Ji Y. Recent development in chemical depolymerization of lignin: A review. *Journal of Applied Chemistry*. 2013;**2013**:1-9. DOI: 10.1155/2013/838645

- [15] Gillet S, Aguedo M, Petitjean L, Morais ARC, da Costa Lopes AM, Łukasik RM, Anastas PT. Lignin transformations for high value applications: Towards targeted modifications using green chemistry. *Green Chemistry*. 2017;**19**:4200-4233. DOI: 10.1039/C7GC01479A
- [16] Espacenet [Internet]. 2017. Available from: https://www.worldwide.espacenet.com/search; Results?ST=singleline&locale=en_EP&submitted=true&DB=&query=lignin+depolymerization&Submit=Search [Accessed: 2017-11-07]
- [17] Wayman M, Lora JH. Process for depolymerization and extraction of lignin [Patent]. Canada. CA 1147105; 1983
- [18] Joshi SS, Kulkarni BD, Tomer AS, Jadhav MR. A Continuous process for depolymerization of lignin to industrially useful chemicals [Patent]. Council of Scientific and Industrial Research. WO 2014/068590 A1; 2014
- [19] Seayad J, Saravanan G, Ramalingam B. Process for the depolymerization of lignin under neutral oxidative conditions [Patent]. Singapore: Agency for Science, Technology and Research. WP 2017/171652 A1; 2017
- [20] Shabtai JS, Zmierczak WW, Chornet E. Process for conversion of lignin to reformulated, partially oxygenated gasoline [Patent]. US 6172272; 2001
- [21] Zmierczak WW, Miller JD. Processes for catalytic conversion of lignin to liquid bio-fuels and novel bio-fuels [Patent]. US 7964761 B2. University Of Utah Research Foundation; 2011
- [22] Shabtai J, Zmierczak WW, Chornet E, Johnson D. Process for converting lignins into a high octane blending component [Patent]. US 20030115792 A1; 2003
- [23] Chaudharyab R, Dhepe PL. Solid base catalyzed depolymerization of lignin into low molecular weight products. *Green Chemistry*. 2017;**19**:778-788. DOI: 10.1039/C6GC02701F
- [24] Gasser CA, Hommes G, Schäffer A, Corvini PF. Multi-catalysis reactions: New prospects and challenges of biotechnology to valorize lignin. *Applied Microbiology and Biotechnology*. 2012;**95**(5):1115-1134. DOI: 10.1007/s00253-012-4178-x
- [25] Crestini C, Crucianelli M, Orlandi M, Saladino R. Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers. *Catalysis Today*. 2010;**156**(1-2):8-22. DOI: 10.1016/j.cattod.2010.03.057
- [26] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chemical Reviews*. 2006;**106**(9):4044-4098. DOI: 10.1021/cr068360d
- [27] Kang S, Li X, Fan J, Chang J. Hydrothermal conversion of lignin: A review. *Renewable and Sustainable Energy Reviews*. 2013;**27**:546-558. DOI: 10.1016/j.rser.2013.07.013
- [28] Schmiedl D, Endisch S, Pindel E, Rückert D, Reinhardt S, Unkelbach G, Schweppe R. Base catalyzed degradation of lignin for the generation of oxy-aromatic compounds—Possibilities and challenges. *Erdöl Erdgas Kohle*. 2012;**128**(10):357-363

- [29] Lavoie JM, Baré W, Bilodeau M. Depolymerization of steam-treated lignin for the production of green chemicals. *Bioresource Technology*. 2011;**102**(7):4917-4920. DOI: 10.1016/j.biortech.2011.01.010
- [30] Jensen MM, Madsen RB, Becker J, Iversen BB, Glasius M. Products of hydrothermal treatment of lignin and the importance of ortho-directed repolymerization reactions. *Journal of Analytical and Applied Pyrolysis*. 2017;**126**:371-379. DOI: 10.1016/j.jaap.2017.05.009
- [31] Katahira R, Mittal A, McKinney K, Chen X, Tucker MP, Johnson DK, Beckham GT. Base-catalyzed depolymerization of biorefinery Lignins. *ACS Sustainable Chemistry & Engineering*. 2016;**4**(3):1474-1486. DOI: 10.1021/acssuschemeng.5b01451
- [32] Miller JE, Evans L, Littlewolf A, Trudell DE. Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Fuel*. 1999;**78**(11):1363-1366. DOI: 10.1016/S0016-2361(99)00072-1
- [33] Roberts VM, Stein V, Reiner T, Lemonidou A, Li X, Lercher JA. Towards quantitative catalytic lignin depolymerization. *Chemistry: A European Journal*. 2011;**17**(21):5939-5948. DOI: 10.1002/chem.201002438
- [34] Toledano A, Serrano L, Labidi J. Organosolv lignin depolymerization with different base catalysts. *Journal of Chemical Technology and Biotechnology*. 2012;**87**(11):1593-1599. DOI: 10.1002/jctb.3799
- [35] Rodriguez A, Salvachúa D, Katahira R, Black BA, Cleveland NS, Reed M, Smith H, Baidoo EEK, Keasling JD, Simmons BA, Beckham GT, Gladden JM. Base-catalyzed depolymerization of solid lignin-rich streams enables microbial conversion. *ACS Sustainable Chemistry & Engineering*. 2017;**5**(9):8171-8180. DOI: 10.1021/acssuschemeng.7b01818
- [36] Erdocia X, Prador R, Corcuera MA, Labidi J. Effect of different organosolv treatments on the structure and properties of olive tree pruning lignin. *Journal of Industrial and Engineering Chemistry*. 2014;**20**(3):1103-1108. DOI: 10.1016/j.jiec.2013.06.048
- [37] Beauchet R, Monteil-Rivera F, Lavoie JM. Conversion of lignin to aromatic-based chemicals (L-chems) and biofuels (L-fuels). *Bioresource Technology*. 2012;**121**:328-334. DOI: 10.1016/j.biortech.2012.06.061
- [38] Pufky-Heinrich D, Rößiger B, Röver R, Unkelbach G. Process scale-up for the production of bioaromatic compounds from lignin. *Chemie Ingenieur Technik*. 2016;**88**(9):1229-1230. DOI: 10.1002/cite.201650156
- [39] Unkelbach G, Schmiedl D, Graf J, Schweppe R. Untersuchung der hydrothermalen Spaltung von Lignin/Produktabtrennung. *Chemie Ingenieur Technik*. 2008;**80**(9):1269-1270. DOI: 10.1002/cite.200750476
- [40] Rinaldi R, Jastrzebski R, Clough MT, Ralph J, Kennema M, Bruijninx PCA, Weckhuysen BM. Paving the way for lignin valorisation: Recent advances in bioengineering, bio-refining and catalysis. *Angewandte Chemie*. 2016;**55**(29):8164-8215. DOI: 10.1002/anie.201510351

- [41] Kozliak EI, Kubátová A, Artemyeva AA, Nagel E, Zhang C, Rajappagowda RB, Smirnova AL. Thermal liquefaction of lignin to aromatics: Efficiency, selectivity, and product analysis. *ACS Sustainable Chemistry & Engineering*. 2016;**4**(10):5106-5122. DOI: 10.1021/acssuschemeng.6b01046
- [42] Mattsson C, Andersson SI, Belkheiri T, Åmand LE, Olausson L, Vamling L, Theliander H. Using 2D NMR to characterize the structure of the low and high molecular weight fractions of bio-oil obtained from LignoBoost™ kraft lignin depolymerized in sub-critical water. *Biomass and Bioenergy*. 2016;**95**:364-377. DOI: 10.1016/j.biombioe.2016.09.004
- [43] Toledano A, Serrano L, Pineda A, Romero AA, Luque R, Labidi J. Microwave-assisted depolymerisation of organosolv lignin via mild hydrogen-free hydrogenolysis: Catalyst screening. *Applied Catalysis B: Environmental*. 2014;**145**:43-55. DOI: 10.1016/j.apcatb.2012.10.015
- [44] Vigneault A, Johnson DK, Chornet E. Base-catalyzed depolymerization of lignin: Separation of monomers. *Canadian Journal of Chemical Engineering*. 2007;**85**(6):906-916. DOI: 10.1002/cjce.5450850612
- [45] Greminger DC, Burns GP, Lynn S, Hanson DN, King CJ. Solvent extraction of phenols from water. *Industrial & Engineering Chemistry Process Design and Development*. 1982;**21**(1):51-54. DOI: 10.1021/i200016a010
- [46] Long J, Zhang Q, Wang T, Zhang X, Xu Y, Ma L. An efficient and economical process for lignin depolymerization in biomass-derived solvent tetrahydrofuran. *Bioresource Technology*. 2014;**154**:7-10. DOI: 10.1016/j.biortech.2013.12.020
- [47] Europa HORIZON 2020 [Internet]. 2017. Available from: https://ec.europa.eu/research/participants/data/ref/h2020/wp/2014_2015/annexes/h2020-wp1415-annex-g-trl_en.pdf. [Accessed: 2017-11-22]
- [48] Nguyen TDH, Maschietti M, Belkheiri T, Åmand EL, Theliander H, Vamling L, Olausson L, Andersson SI. Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water. *Journal of Supercritical Fluids*. 2014;**86**:67-75. DOI: 10.1016/j.supflu.2013.11.022
- [49] Beckham GT, Biddy MJ, Chmely SC, Sturgeon M. Hydroxide catalysts for lignin depolymerization [Patent]. US 20140107381 A1; 2014
- [50] Beckham GT, Biddy MJ, Chmely SC, Sturgeon M. Hydroxide Catalyst for lignin depolymerization [Patent]. US 9631146 B2; 2017
- [51] Cheng F, Brewer CE. Producing jet fuel from biomass lignin: Potential pathways to alkyl-benzenes and cycloalkanes. *Renewable and Sustainable Energy Reviews*. 2017;**72**:673-722. DOI: 10.1016/j.rser.2017.01.030
- [52] Kleinert M, Barth T. Phenols from lignin. *Chemical Engineering & Technology*. 2008; **31**(5):736-745. DOI: 10.1002/ceat.200800073

- [53] Rutten C, Ramirez A, Duque JP. Hydrotreating and hydrothermal treatment of alkaline lignin as technological valorization options for future biorefinery concepts: A review. *Chemical Technology and Biotechnology*. 2017;**92**(2):257-270. DOI: 10.1002/jctb.5103
- [54] Long J, Xu Y, Wang T, Yuan Z, Shu R, Zhang Q, Ma L. Efficient base-catalyzed decomposition and in situ hydrogenolysis process for lignin depolymerization and char elimination. *Applied Energy*. 2015;**141**:70-79. DOI: 10.1016/j.apenergy.2014.12.025
- [55] Zhang S, Liu L, Fang G, Yan N, Ren S, Ma Y. Hydrogenolysis and activation of soda lignin using [BMIM]Cl as a catalyst and solvent. *Polymer*. 2017;**9**(7):279. DOI: 10.3390/polym9070279
- [56] Zmierczak WW, Miller JD. Processes for catalytic conversion of lignin to liquid bio-fuels and novel bio-fuels [Patent]. US 8299310 B2; 2012
- [57] Liu CF, Chen CC, Chen C, YU PJ, Chang YH, Wan HP, Lee HT. Method for preparing phenolic compounds [Patent]. US 8648218; 2014
- [58] Fernández-Rodríguez J, Erdocia X, De Hoyos-Martinez PL, Alriols M, Labidi J. Small phenolic compounds production from Kraft black liquor by lignin depolymerization with different catalytic agents. *Chemical Engineering Transactions*. 2017;**57**:133-138. DOI: 10.3303/CET1757023
- [59] Van den Bosch S, Schutyser W, Vanholme R, Driessen T, Koelewijn SF, Renders T, De Meester B, Huijgen WJJ, Dehaen W, Courtin CM, Lagrain B, Boerjan W, Sels BF. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy & Environmental Science*. 2015;**8**(6):1748-1763. DOI: 10.1039/C5EE00204D
- [60] Renders T, Van den Bosch S, Koelewijn SF, Schutyser W, Sels BF. Lignin-first biomass fractionation: The advent of active stabilisation strategies. *Energy & Environmental Science*. 2017;**10**(7):1551-1557. DOI: 10.1039/C7EE01298E

IntechOpen