Hydrothermal base catalyzed depolymerization and conversion of technical lignin – An introductory review

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HIGHLIGHTS

- Valorization of technical (Kraft-)lignin by base catalyzed hydrothermal processes.
- Process development and background for the generation of valuable aromatics.
- Relevant for chemist, engineers and biomass conversion scientists in general.

ABSTRACT

Lignin represents the most significant potential source of sustainable aromatic compounds. Currently, the vast majority of technical lignin could be sourced from industrial paper production and in particular the Kraft process, where it is conventionally combusted for chemicals recovery and heat generation (e.g. for plant operation). While in recent years several efforts have concerned the conversion of native lignin (i.e. as found in nature) during biomass processing, there has also been significant focus on the "Base Catalyzed" conversion of technical lignin. This process is of significant interest, since it could be potentially integrated into existing Kraft mill infrastructure. The following review paper focuses on the development of the hydrothermal base catalyzed depolymerization (HBCD) of lignin, as a basis to produce valuable chemical compounds. Focus will be placed on NaOH catalyzed reactions in the aqueous phase, as this approach is considered the most promising. Focus is placed on reaction conditions and characterization of monomeric aromatic compounds from the HBCD approach. Oligomers, as largest product fraction, is also considered, however, these are seldom analyzed in detail in the literature and ideas on further use are scarce. The review also addresses findings in literature concerning the assessment of the solid, liquid, and gas product streams arising from HBCD. From this paper, process conditions for HBCD reactions can be derived and it is shown that the solid phase has a high potential for further valorization and downstream processing.

1. Introduction

The extensive usage of fossil reserves and establishment over the last century or so of associated industries to provide energy and industrial chemicals for a variety of consumer products (e.g. plastics) has resulted in a strong dependency on these finite feedstocks. These fossils, as a consequence of the geochemical processes that formed them, are highly condensed carbon-based materials, where a significant quantity of carbon is bound and their use as an energy carrier results in the emission of CO_2. In this context, the EU has decided to cut primary energy consumption until 2020 by 20% (relative to 1990), whilst the US Department of Energy (DOE) has a performance goal for new fossil power plants having 60% efficiency (coal HHV-AC) with $\geq 90\%$ CO_2 capture [1,2]. These positions have been further strengthened by the ratification of agreements such as COP21 [3]. As a consequence of such agreements and frameworks there is an ever increasing awareness of

global climate change and its consequences. To reach the aforementioned targets and ultimately establish a sustainable chemical/energy economy, the use of renewable resources will be of critical importance.

One considered approach to address these challenges is to re-invigorate our society's and industrial interest regarding the use of lignocellulosic biomass as a platform for chemicals, fuel, and energy production [4]. Lignocellulose will be the main precursor for biofuel production in envisioned 2nd and 3rd generation Biorefineries, whilst further value is expected to be derived from the lignin component (composed of interlinked phenyl-propanoids; Fig. 1), through the production of aromatics. However, as highlighted in previous reviews and reports, the quantitative and selective production of these compounds represents a significant chemical challenge [5]. At the time of writing, one of the main industries currently involved in biomass conversion (i.e. for non-food applications) is the pulp and paper industry. The United Nations Food and Agricultural Organization estimates a total

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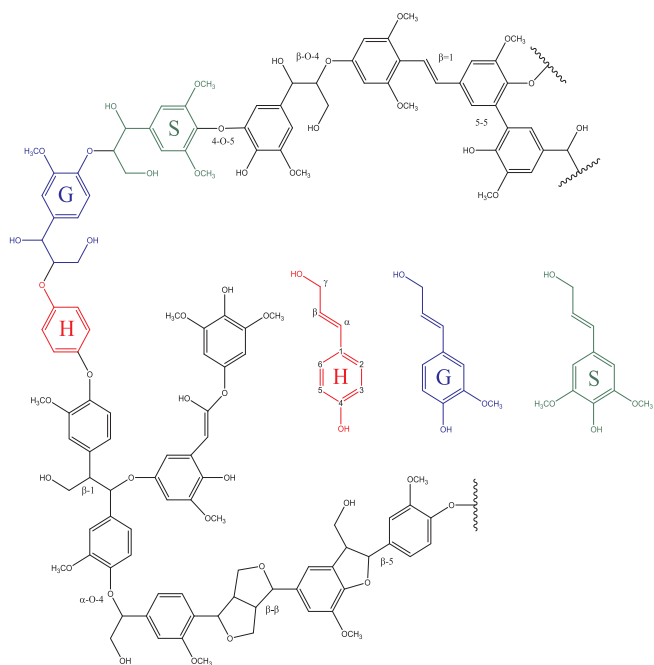
Fig. 1. Structure of native lignin with description of the most common bonds. The three generic phenyl propane building blocks are given on the right and highlighted in the structure: (H) p-hydroxyphenyl, (G) p-guaiacyl, (S) p-syringyl.

capacity of *ca.* 160 Mt/a (2016) of dried wood pulp is used in the production of paper and paperboard [6]. The main process for producing pulp is the "*Kraft*" process, accounting for *ca.* 90% of virgin pulp [7]. In this process cellulose is separated from the other wood constituents (i.e. hemicellulose, lignin, and extractives) based on thermal treatment in NaOH (aq) and Na_2S (aq) at *ca.* 170 °C for 2 h [8]. With a pulp yield of 45 wt.% this accounts for yearly usage of wood in the pulp & paper industry of *ca.* 350 Mt [8]. During a complex recovery process to recycle the chemicals used, the lignin and hemicellulose mixture, commonly referred to as "Black Liquor", is typically burnt to generate process heat and additional steam for power generation [7].

With regard to chemistry, the dissolved lignin in the black liquor consists predominantly of substituted aromatic units of varying molecular weight. As such this stream represents an interesting base e.g. for the production of plastics and carbon fibers, and also potentially for liquid fuels [9–19]. However, the utilization of this lignin for the production of chemicals and fuels is complicated due to the complexity and heterogeneous chemistry of the lignin "molecule" and Black Liquor. In this regard, the type and quality of wood and the technical process used to separate its constituents strongly influence the chemical nature of the resulting lignin-derived product stream [20]. The development of a chemical process that facilitates the selective breakdown of different lignin to chemicals and fuels in an economically attractive manner represents perhaps the most significant challenge with regard to establishing a holistic Biorefinery [5].

In this context, this review paper deals with the development of the hydrothermal base catalyzed depolymerisation (HBCD) processes as applied to the conversion of technical lignin. The review focuses on HBCD as a platform for the production of valuable chemical compounds including aromatics (e.g. phenolics) from such technical lignins. Focus will be placed on NaOH catalyzed reactions in the aqueous phase, as this approach is considered most promising when considering incorporation into Kraft mill plant architecture. A short description of technical lignins is provided followed by discussion of developed HBCD-based processes particularly suited to the dissolution of Kraft lignin (e.g. high pH, solubility etc.). This is complimented by a description of the reported products and their valorization opportunities.

Attention is given to the production, characterization and optimization of monomeric/oligomeric aromatic compounds from the HBCD approach. The oligomeric product is of particular interest regarding valorization as this fraction typically comprises *ca.* 75 wt.% of the feed and its efficient utilization will be of importance regarding market development and complete biomass utilization. In the context the possibility to adjust/optimize upstream processing, in order to generate an as homogeneous lignin-derived stream as possible, is also of interest [21]. Furthermore, in this review, conversion reactions performed in organic (alcoholic) solvents, mainly CH_3OH and CH_3CH_2OH will be discussed. Regarding characterization and analytics, a wide of variety of techniques have been applied including a number of Nuclear Magnetic Resonance (NMR) spectroscopy methods (^{1}H, ^{13}C, ^{31}P, 2D techniques) have been developed, alongside Infra-Red spectroscopy (FT-IR), Pyrolytic-Gas Chromatography-Mass Spectrometry (pyro-GC-MS) and Size Exclusion Chromatography (SEC) [22,23]. The analytical information afforded by each technique will be discussed in context.

2. Technical lignins

A technical lignin is described as a lignin as sourced from a large scale industrial process. Lignin of this type can be sourced either directly (e.g. lignosulfonates from the sulfite process) or in solution (e.g. Kraft lignin (denoted hereon as KL)). In the context of KL, particularly from a process standpoint, the LignoBoost® process is of note, having been recently installed at two paper mills (2013: Domtar Plymouth NC, USA and 2015: Stora Enso, Sunila, Finland), capable of generating *ca.* 100 kt/a(KL). Precipitation of lignin from the black liquor is advantageous regarding effective integration of the recovery boiler and pulp mill, leading to improved power generation efficiency (e.g. *via* gasification for usage in a turbine) [24,25]. This leads to improved plant costings and recapitalization of the LignoBoost® installation. Continued adoption of this technology will in turn lead to increased availability of KL in the future. The implementation of KL conversion technologies at Kraft pulp mills has the aim to transform recovered lignin from a waste stream into a chemical commodity, generating a potentially higher value product (e.g. than simply being combusted). However, there remains firstly the chemical challenge (e.g. selective deconstruction of lignin) and secondly the commercial challenge (e.g. relatively low price of current aromatic feedstocks). The diversity of both native and technical lignin structure making the design of one global, all-encompassing process applicable at all mills a significant undertaking, and likewise it is worth noting that KL is not the only viable feedstock for chemical and fuel production. Other options include steam exploded lignin, organosolv lignin, or ball milled lignin [26–31]. However, the availability of these other lignins can be considered to be limited in the short term, it is expected that in the long term the development of alternative pulping techniques will slowly come online (e.g. with the concurrent development of "Organosolv" pulping at the pilot scale based on $CH_3CH_2OH:H_2O$ mixtures and Alcell Lignin [32,33]. While currently not particularly cost competitive, the "Organosolv" process potentially can deliver sulfur-free lignin which could be more easily processed with heterogeneous catalysis [34–36].

With regard to the utilization of lignin of different origins, Constant et al. have recently investigated softwood KL (Indulin AT), soda lignin and four different organosolv lignins [22]. Transition metal (e.g. Ni) catalysts were employed in nanoparticulate form for the hydrogenolysis of lignin [36–53], leading to a complex product range. This approach was reported to produce low cost synthetic fuels, with the authors indicating this product could contribute to *ca.* 10% of a global fuel supply (i.e. in combination with 2nd generation Biorefineries) [54]. Treating lignin with H_2 (e.g. as supplied in-situ) has been reported as potential route to produce phenol derivatives, although further kinetic studies are required [41,49,55,56]. Regarding complete lignocellulosic biomass conversion, processing under alkaline conditions typically leads to the production of a lignin stream, the properties of which are altered with
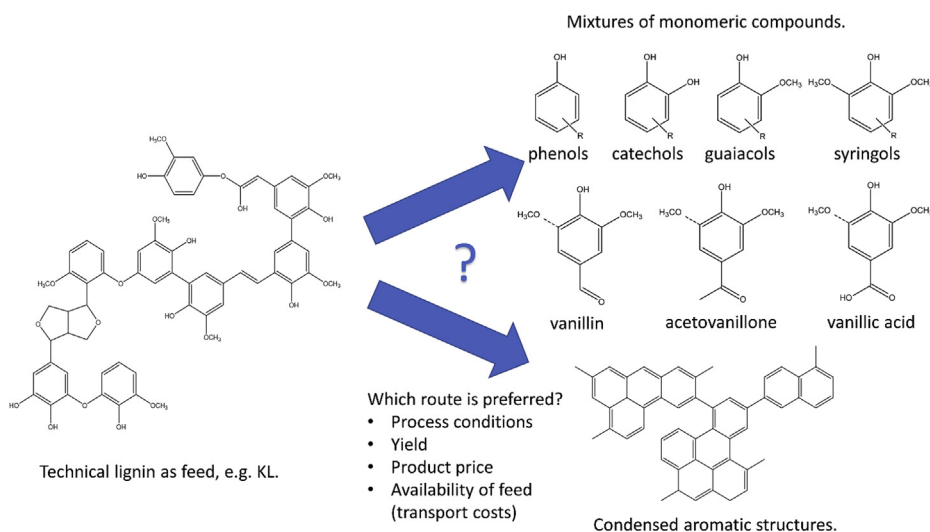
Mixtures of monomeric compounds.

phenols   catechols   guaiacols   syringols

vanillin   acetovanillone   vanillic acid

Technical lignin as feed, e.g. KL.

?

Which route is preferred?
- Process conditions
- Yield
- Product price
- Availability of feed
  (transport costs)

Condensed aromatic structures.

Fig. 2. Possible routes for the upgrading of technical lignin. In literature, monomeric compounds are the preferred target molecules. A process with defined oligomeric structures can result in higher yield and even higher value products. This is a function of feed structure, process conditions, yield of desired products, the product price, and the availability of the potential feed.
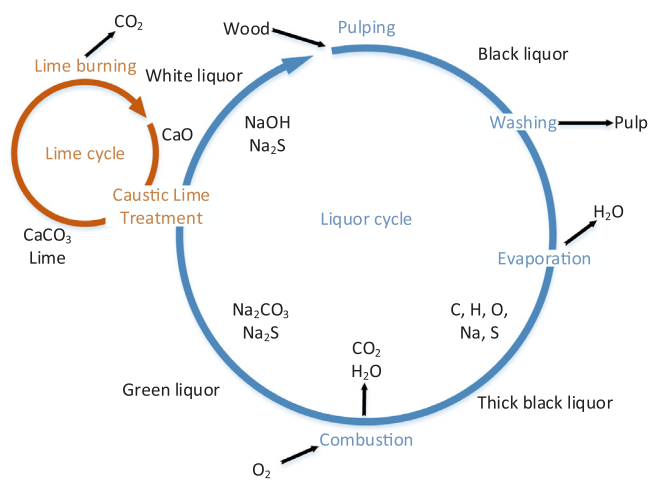

Fig. 3. Liquor and lime cycle of a Kraft mill. Removal of lignin *via* e.g. LignoBoost® will take place between evaporation and combustion. Using a NaOH (aq) based process will lead to the addition of water into the process and increase energy consumption, while no new chemicals for recovery are added.

respect to the physicochemical properties of the native "parent" lignin [22]. It has been observed that the number of β-ether linkages is reduced to *ca.* 15% relative to the original lignin, with C–C linkages becoming increasingly predominant in the structure (Fig. 2) [21]. Therefore, for lignin to serve as a renewable feedstock for chemical and fuel provision there remains the demand for efficient and selective depolymerization or other forms of upgrading. As a consequence of this discussion and to highlight the possibilities of lignin conversion through industrially near processes, the use of base/alkaline catalysts and in particular NaOH catalyzed processes are of interest. While also other bases can be used, NaOH is of interest as it can be regenerated in the mill's own recovery cycle and is available in a Kraft mill in high amounts (Fig. 3) [7]. As will be discussed alongside the classical Brønsted base, additives (e.g. boric acid or phenol as capping agents) have also been investigated [57,58].

3. Hydrothermal base catalyzed depolymerization

In this review, a base catalyzed depolymerization process is defined as a process where a Brønsted or Lewis base is present in a liquid solvent (e.g. water). The nucleophile, an electron donor such as HO⁻, interacts with the reactant resulting in most cases in proton withdrawal. The HBCD process relies on mainly Brønsted basicity. Deprotonation of

OH groups of phenolics and other aromatics subunits of lignin alter the electronic structure of these moieties and facilitates solubility in H_2O [59–61]. This shift in charge destabilizes other linkages in the molecule encouraging bond cleavage and ultimately depolymerization. It has been reported that a minimum of 31 phenolic OH groups per 100 phenyl-propane units are required for lignin solubilization in aqueous alkali media [62]. The reaction pathway is influenced by solvent choice, catalyst type, and temperature. The latter parameter is of interest (along with pH) as it not only enhances reaction rate but also alters the reaction solvent properties (e.g. ionic product, dipole moment of H_2O, *etc.*) [60].

HBCD has been described for numerous biomass-derived model compounds [29,63–67], and underpins the Kraft pulping process (where wood chips are cooked in NaOH/Na_2S mixtures at *ca.* 170 °C for 2 h [8]. Regarding lignin conversion and HBCD Rößiger et al. provide a good overview on general products, reaction conditions, and possible applications [68]. This paper aims at giving detailed information on reaction conditions, analytical means, and detailed products' information including mass balances in order to enable fellow researchers to set their own conditions *via* a data-driven approach. In 1994 Thring investigated the conversion of Alcell lignin with NaOH (aq), with liquid phase products obtained in yields of ≤30% [69]. HBCD has also been envisioned as pre-treatment step to produce a product mixture more suitable for further processing (e.g. catalytic hydrodeoxygenation for gasoline-range aromatic fuel production) [12,70–75]. Peng et al. also proved the effectiveness of base catalyzed depolymerization during pyrolysis of lignin as residue from black liquor producing mainly –OCH_3 free phenols between 350 and 550 °C [76].

Regarding the mechanism of HBCD, Gierer et al. have described the reaction mechanisms occurring at specific lignin subunits during Kraft pulping [77], with particular detail provided regarding the depolymerization of β-O-4 and α-O-4 model compounds in 2 M NaOH (aq) and a mixture of NaOH (0.875 M (aq)) and Na_2S (0.129 M (aq)). This was performed to simulate the white liquor conditions found typically in the Kraft process [63–65]. Reactions were conducted at 170 °C for 2 h and resulted in moderate to complete cleavage of β-O-4 bonds. It was reported that the cleavage of the α-O-4 linkage could only be achieved with addition of Na_2S [64]. In the former process, the reaction pathway for β-O-4 cleavage in the presence of HO⁻ or HS⁻, both start *via* nucleophilic attack and subtraction of a proton from the phenolic end group, thereby altering the electronic structure of the compound (Fig. 4). As a consequence, it is proposed that ether bonds are broken at the C_α position, resulting in the appearance of a quinone methide intermediate. In NaOH (aq), the C_β is subsequently deprotonated to form an enol-ether which is, to a large extent, stable under alkali conditions.
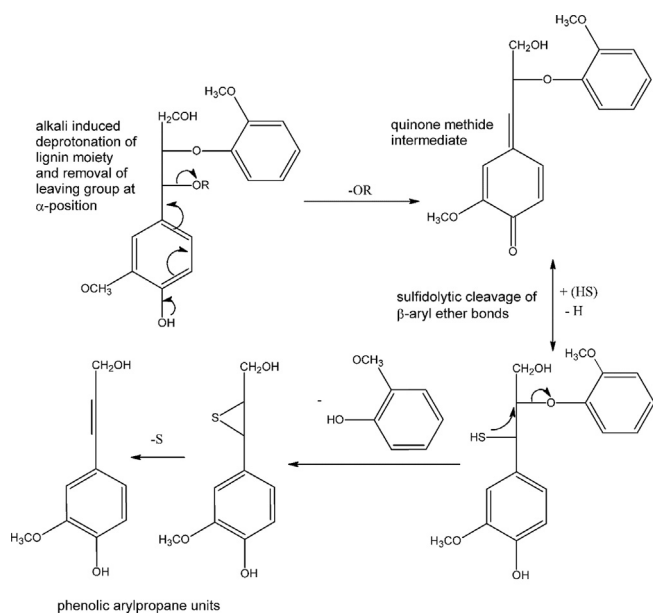
Fig. 4. Lignin cleavage mechanism under Kraft process conditions. (Reproduced with permission from Ref. [77]).

The addition of Na_2S (and in turn sulfide ions) to the reaction mix results in the addition of sulfur at the C_α/quinone methide structure, which leads to displacement of the aroxyl substituent at the C_β position, leading to the formation of an epi-sulfide intermediate and a phenolic hydroxyl group [77]. Typically these initial mechanistic studies were performed at temperatures and conditions relevant to the Kraft pulping

process [63–65,77]. Clearly, in such reaction schemes, the strength of the employed base will play a crucial role. In this context, Miller et al. reported on the use of a number of bases and showed that stronger bases (e.g. KOH, NaOH) are able to produce higher yields of low molecular weight species than weaker bases (e.g. LiOH) [78–80].

With medium temperature alkali processes, the HBCD process is performed at temperatures between 150 and 350 °C, typically together with an electron donating additive in a selected solvent. It has been reported that propanoid side chains (between 230 and 260 °C) and C–C and β-β bonds (between 275 to 330 °C) can be broken down [81]. Under these conditions increased re-polymerization and condensation are also observed, as seen by the increased yield of insoluble components after reaction. Independently of the chosen reaction temperature, H_2O is most commonly used as solvent and HO^- is the electron donating species. There have been other reports that indicate the use of high temperatures/pressures and/or solvents in the supercritical (sc) phase (e.g. CO_2, CH_3OH and CH_3CH_2OH), these processes are not within the scope of this review [82–84].

It has been observed that longer reaction times lead to an increase in the average molecular weight of the product sample, suggesting a degree of re-polymerization (e.g. via condensation reactions). In this context, the use of KL is interesting as it has already undergone a base catalyzed conversion process, rendering the resulting KL devoid of or featuring limited amounts of α-O-4 and β-O-4 structural linkages. Similarly, organosolv lignin has reduced amounts of β-ether linkages, dependent on the severity of the employed process [21]. In this context, Erdocia et al. have reported yields of 13–19 wt.% (with yield defined as $y_i = \frac{m_{oil} - m_{oil,start}}{m_{lignin,start}}$) for different organosolv lignins after treatment under a base catalyzed process at 300 °C for 80 min in 1 M NaOH (aq); comparable to other base catalyzed processes [28]. In this report, the retention time was quite long, which could have led to the observed
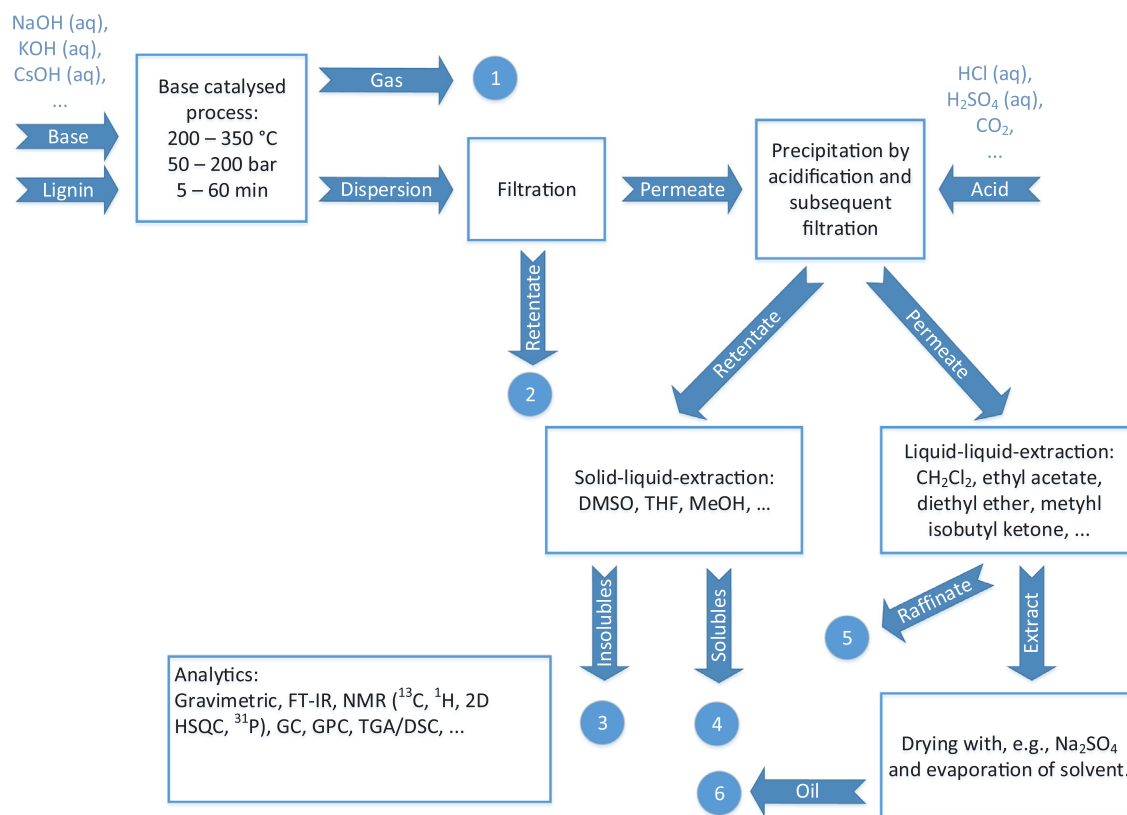

Fig. 5. Process overview for a typical base catalyzed reaction performed in aqueous phase. The gas phase ① is directly separated and the product after reaction is filtered and solid compounds are washed, leading to retentate ②. The permeate is acidified with HCl (aq), H_2SO_4 (aq), or CO_2 and subsequently filtered. The retentate is subjected to a solid-liquid-extraction and the permeate to liquid-liquid-extraction. This leads to the fractions ③, ④, and ⑥. The raffinate ⑤ is commonly not analyzed and the liquid-liquid-extraction is performed repetitive until the feed is colorless. The analytics depend on the actual phase, i.e. solid, liquid, or gas.

higher degree of (re-)polymerization.

Another important factor in the comparison of lignin conversion results is the consideration of the manner in which the products have been obtained. For example, most reported procedures include an acidification of the product stream, followed by a filtration step (Fig. 5). The "oil" product is then extracted from the low pH solution *via* an organic solvent (e.g. ethyl acetate) and, in some cases, the solids are also subsequently extracted (e.g. using THF or DMSO), leading to what is commonly described as the dissolvable and non-dissolvable product streams. In the literature, the latter is often referred to as "coke", while the former is described as "unreacted lignin" – this description is slightly misleading, as the product is probably not unreacted. Particular reference and consideration to these points will also be made during the course of this review.

4. Examples of HBCD as applied to technical lignins

Conducting the HBCD of lignin is of particular interest as such a process could be integrated into existing Kraft mills. H_2O is still in the subcritical state up to 370 °C, whereby an increased ionic product with increasing temperature favors ionic reaction pathways [85–87]. Furthermore, the dielectric constant decreases nearly linearly with temperature, but the dissolution of salts is still significant enough at elevated temperatures that precipitation does not readily occur, as assisted by the relatively high density [85,87]. Precipitation of solids under the applied reaction conditions would impede the use of a continuous reactor and development of more industrially relevant continuous processing.

4.1. Technical lignins and the challenge of comparing different approaches

The composition of a technical lignin is dependent on the process from which it is derived (e.g. Kraft or Organosolv, and the specific process conditions) and also its geo-/biological origin (e.g. hardwood or softwood, subspecies, *etc.*). In general, hardwood lignin can be regarded as rich in syringyl and guaiacyl units, while softwood typically contains only guaiacyl units [88]. In this context, a report concerning the application of different bases to Alcell Organosolv lignin of mixed hardwoods and different model compounds was conducted by Miller et al. in CH_3OH, CH_3CH_2OH, and H_2O as solvent [78,80]. Strong bases (i.e. NaOH, KOH, and CsOH) were reported to provide better results than weak bases (e.g. $Ca(OH)_2$ and Na_2CO_3). In the alcohols CH_3OH and CH_3CH_2OH, an excess of strong base was found to be necessary, as the solvents were transformed into formic acid and acetic acid, respectively, thus neutralizing the base (and inhibiting the catalyzed pathway) [80].

Regarding HBCD and the applied conditions for technical lignin conversion, reactions are commonly conducted in 4 wt.% (1 M) NaOH (aq), usually containing *ca.* 5–10 wt.% of dissolved lignin. The reaction temperature is usually found in the range of *ca.* 250–350 °C, but some reports indicate the use of temperatures as low as 150 °C or as high as 400 °C (e.g. scH_2O in batch reactors; Table 1) [28,30,31,58,78,89–93]. Determining accurate reaction kinetics relies on the ability to determine accurate conversion of the employed lignin. This is often inhibited by a problematic quantification of the (unconverted) lignin and/or intermediates. Furthermore, complications can arise regarding non-dissolvable solids (e.g. those not recovered using THF, DMSO, or acetone), that remain after acidification/filtration, and which are often declared as "unconverted" or "unreacted" lignin [28,31,58,93]. It is possible that this lignin has been chemically modified as a consequence of processing, and is merely not dissolvable in the solvents used.

Regarding different types of technical lignin, the results from investigations employing KL and Organosolv lignin are rather similar. In this context, the umbrella description of an Organosolv process includes different solvents, normally low molecular weight alcohols (CH_3OH or CH_3CH_2OH), or formic acid, acetone, *etc.* in combination with H_2O.

Table 1
Overview of reactions with lignin in NaOH (aq) basic environment.

| Source	Lignin	Concentration [wt.%]		Temperature [°C]	Retention Time [min]	Process
		NaOH	Lignin			
#1 [89]	Kraft (Indulin AT, mixed softwood)	5	10	270, 290, 315	13, 23, 43	Continuous (102 mL)
#2 [28]	Organosolv (acetosolv, formosolv, aceto/formosolv)	4	5	300	80	batch (V ??)
#3 [30]	4 different corn stover enzymatic lignins, 1 Kraft lignin	2, 4	10	270, 300, 330	40 (+8–12 min preheating)	batch (50 mL)
#4 [31]	hemp and softwood lignin (FIRSST process, see: [111])	5	10	300, 310, 320, 330	45 min (including heat up time)	batch (15 mL)
#5 [90]	Kraft Lignin (softwood)	4.6, 5.0, 5.4, 6.6	20	200, 250, 300, 350	30, 45, 60, 90, 120, 180, 240	batch (100 mL)
#6 [91]	Organosolv lignin and two types of hydrolytic lignin	10	10	165, 210, 290, 350	15, 60 (+45 to 60 min heat up time)	batch (500 mL)
#7 [58]	Organosolv lignin	2 to 5		240, 260, 280, 300, 320, 340	2.5, 5, 10, 15	continuous (V ??)
#8 [92]	Organosolv lignin (beech wood saw dust - > hardwood) sulfur containing technical lignin	1, 3, 5	5	organosolv: 250, 300, 350 technical lignin: 300, 320, 340	5, 10, 15	continuous (ca. 120 mL)
#9 [78]	Organosolv from mixed hardwood (Alcell process)	1 to 10	10	290, 310, 330	5, 10, 15, 30, 45, 60	batch (15 mL) only mass balances on ether solubles
#10 [93]	Organosolv lignin (olive tree pruning)	4	5	300	40	batch (V ??)
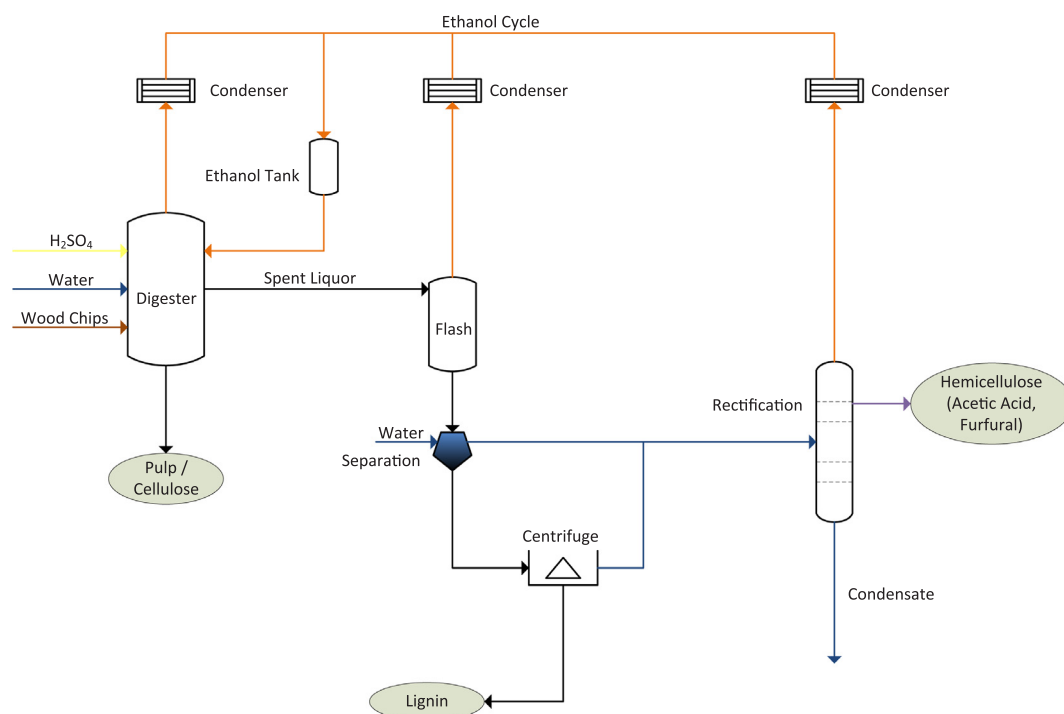
Fig. 6. Exemplary Organosolv process description based on ethanol:H_2O as solvent. Typical process conditions for the digester are: ethanol:H_2O 6:4, ϑ = 180–200 °C and τ = 2–4 h. Addition of ca. 1 wt.% H_2SO_4 gives increased delignification and enables a 30 °C lower temperature.

Fig. 6 depicts a typical Organosolv process as described in literature [94–97]. Rinaldi et al. have reported that the Hildebrand solubility parameter of the applied solvent should be in the range of 23 ± 2 $MPa^{1/2}$, comparable to the value reported by Schuerch of 22 $MPa^{1/2}$, as reported in 1952 [62,98]. These solvents in combination with H_2O at different (e.g. weight, molar, *etc.*) ratios plus different retention times and temperatures result in Organosolv lignin with varying properties/characteristics.

Conventionally after a HBCD reaction, the pH of the product mixture is lowered *via* acid addition. Typically HCl (aq) [28,30,31,58,78,89,91–93], or H_2SO_4 (aq) [90], is used on a lab scale but also CO_2 has been used, mainly to emulate industrial conditions like the LignoBoost® process [99]. Table 2 provides an overview of the applied analytics that have been used after reactions provided in Table 1. A reduction in the pH typically leads to precipitation, with the resulting solids recoverable based on filtration or centrifugation and drying. In some reports, an extraction is applied using organic solvents (e.g. DMSO, THF, or acetone), to generate a soluble and insoluble fraction; in turn defined as coke or unreacted lignin [28,31,58,78,90,93]. The acidified aqueous phase has also been known to be extracted using an organic solvent (e.g. ethyl acetate, diethyl ether, methyl isobutyl ketone) [28,31,58,78,89,91–93], with solvent selection influencing the composition of the extracted oil [92]. After drying (e.g. with Na_2SO_4) and evaporation, the oil is typically dissolved in a specific amount of (another) organic solvent and analyzed (e.g. *via* GC–MS and/or FID) [28,30,31,58,89,91–93].

With the aim of selecting comparable conditions and results, which is somewhat of a challenge given the variety of HBCD processes/lignin sources, benchmark conditions 300 °C, 1 M NaOH (aq) (i.e. 4 wt.%), 10 wt.% (lignin loading) have been defined (compare Table 1). As observed in the data provided, retention times vary the most. In some cases, reaction mass balances are far from closed, even when a batch reactor was used [28,31,93], perhaps related to relatively small reaction scale (e.g. 15 mL) [31]. This is further complicated by the formation of difficult to handle products. For example, Miller et al. have observed in some reactions, the formation of a tarry black solid product

which adhered to the reactor wall, making complete mass recovery problematic [80]. Fig. 7 shows the yields of solids (oligomers), oil, and gaseous phase given in Table 3 in a box-whisker plot. Solid yields have been reported in the range from 35 to 93 wt.%, with higher values typically including all ether soluble constituents. Regarding oil yields this can vary from 5.5 to 23 wt.%. Gaseous products are typically limited (e.g. < 1 wt.%) [28,90], although Katahira et al. reported *ca.* 5 to 9.3 wt.%, based on the treatment of KL at 330 °C and 4 wt.% NaOH (aq) [30]. Having used a continuous HBCD system, Beauchet et al. closed the process mass balance difference *via* the gas phase leading to a gas product stream of 15 wt.% of the original lignin [89]. In most cases the gas phase is considered insignificant and is neither determined gravimetrically, nor are its compounds.

4.2. The solid or "residual" phase

The solid residue of HBCD reactions is recovered and dried (e.g. either under vacuum and elevated temperatures, or by freeze drying). The analytical techniques employed in the characterization of the solid phase have been summarized in Table 2 and typically include (amongst others) elemental analysis, GPC/SEC, NMR (^1H, ^{13}C, ^{31}P), Pyro-GC-MS, and FT-IR spectroscopy. In this context, Erdocia et al. have reported on the separation of the solid phase after the HBCD of organosolv lignins (i.e. acetosolv, formosolv and acetosolv/formosolv) based on extraction with THF over 3 h [28]. In the aforementioned report the authors define the dissolvable amount as residual lignin and the non-dissolvable as coke. This residual lignin is then analyzed *via* GPC and Pyro-GC-MS. Erdocia et al. experience a reduction in M_W of 20% for the acetosolv and aceto/formosolv lignin and an increase of 75% for the formosolv lignin. The PDI (M_W/M_N) is increased by *ca.* 50% and 330% respectively [28]. Furthermore, it is reported that the HBCD of formosolv lignin gave the highest proportion of monomeric phenolic compounds in the recovered oil phase (28.19%). Beckham et al. described a reduction of 75% and Schmiedl et al. of 55% in terms of M_w [30,92]. Absolute values for M_W or M_N are not provided in this review as these values are extremely method dependent and cannot be compared

Table 2

Product separation and analytical techniques of the reactions with lignin in basic environment shown in Table 1.

Source	precipitation and acid used	liquid phase	solid phase	comments
#1	pH < 2 with 1 N HCl filtration	Liquid-liquid extraction aqueous phase: HPLC organic phase: GC, mass	Elemental Analysis, 31P NMR, mass	gas phase mass balance by difference -> leads to high gas masses (25 wt.%), probably coke included
#2	pH 1 with 37 wt.% HCl filtration	extraction with ethyl acetate • organic phase: o GC–MS o dried -> MALDI-TOF	extracted with THF for 3 h • undissolved: coke • dissolved: unconverted lignin o SEC o Py-GC-MS	total mass balances: 50–55%
#3	pH 7 with HCl (conc.?) centrifugation	freeze dried • low molecular weight solids o extraction with acetone ▪ GC–MS o extraction with THF ▪ GPC	freeze dried • high molecular weight solids o ^{13}C NMR o extraction with THF ▪ GPC o extraction with acetone ▪ GC–MS	
#4	pH 1.7 with 1 N HCl H2O bath 70 °C, 15 min filtration	extraction with diethyl ether • organic phase o GC–MS • aqueous phase o none	extraction with THF • soluble: oligomers • insoluble: char	
#5	pH 2 with 1 M H2SO4 filtration	TOC-analyzer	acetone extracted acetone soluble polyols (DL) acetone insoluble solid residue (SR) ATR FT-IR 1H NMR Elemental Analysis	
#6	pH 2 with conc. HCl (+32 wt.%) centrifugation	extraction with dichlormethane in centrifuge vial • organic phase o GC-FID • aqueous phase o none	GPC 13C NMR (in DMSO-d6 and NaOH) Elemental Analysis	reactions also done with other bases (NH4OH and KOH)
#7	pH 1 with HCl filtration	repeatedly extracted with ethyl acetate -> dried • oil: o MALDI-ToF o dissolved in 50 mL ethyl acetate: ▪ GC–MS ▪ GC-FID	dried • solids: o weighed o extraction with THF ▪ THF soluble (lignin, high molecular weight products): • elemental analysis • 1H and 13C NMR, 11B NMR ▪ THF insoluble: Coke • elemental analysis	boric acid (H3BO3) was used as capping agent in batch runs ^{11}B NMR only on samples with boric acid spectra of ^{1}H and ^{13}C NMR are not given in paper and results of ^{13}C is also not mentioned in text
#8	pH 3–4 with HCl filtration	extraction with methyl isobutyl ketone (MIBK) • organic phase (MIBK): o GC–MS-FID o SEC o elemental analysis • aqueous phase: o HPLC	washed with H2O and dried on air and vacuum elemental analysis SEC	
#9	pH 2 with HCl refrigerated over night filtration	extraction with ethyl acetate (this separation is only done in one experiment)	dried extracted with diethyl ether -> ether soluble	
#10	pH 1 with HCl filtration	extraction with ethyl acetate -> oil • MALDI-ToF • GC–MS	extraction with THF • THF soluble: residual lignin o HP-SEC • THF insoluble: char	reactions also done with H3BO3 and phenol as capping agent, the yields for the GC analysis of the phenol reactions give more than 100 %, although they are referred to total oil mass

directly between each other [100]. It is important to consider how the solid phase is separated from the HBCD product mixture. In this context, the use of HCl (aq) at different concentrations is typical, with the final pH ranging from 1 to 7 (Table 2). The pK_a of the produced dimeric compounds lies in the range of 7–10 [101], and nearly all of the monomeric compounds are still dissolvable in neutral H2O in their protonated form at the given concentrations. Therefore, an investigation into the stepwise precipitation may provide further information regarding a more detailed product distribution

Analysis *via* ^{13}C NMR, either in the solvated or solid state, and FT-IR

can provide both quantitative and qualitative information. For example, Katahira et al. have reported a decrease in resonances related to methoxyl groups (δ_{13C} = 56 ppm) and an increase in resonances associated with aliphatic groups (δ_{13C} = 40–0 ppm), during ^{13}C CP-MAS solid-state NMR analysis of the four investigated HBCD treated lignin substrates. The aromatic region (i.e. δ_{13C} = 160–110 ppm) also undergoes a significant change towards lower intensity (Fig. 8) [30]. In her doctoral thesis, Valenzuela Olarte presented the ^{13}C NMR analysis of different lignin before and after HBCD treatment in DMSO-*d*6 and 10 wt.% NaOH (aq) [91]. Samples taken after 15 min and 60 min
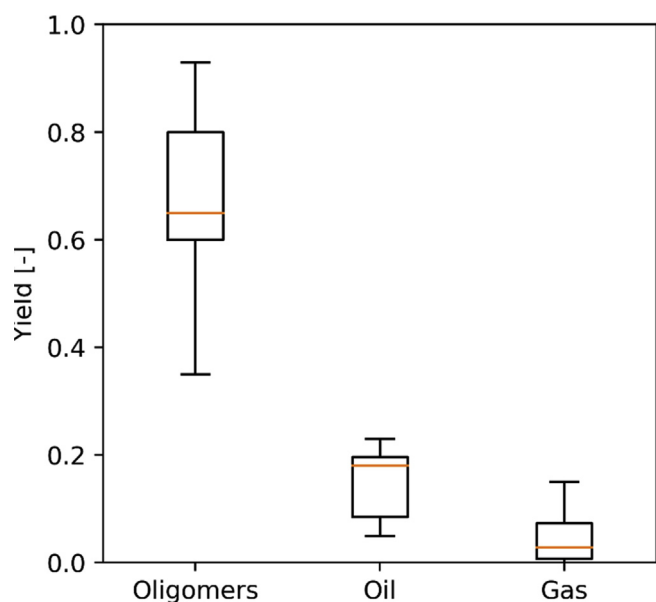
Fig. 7. Box-whisker plot of the yields given in Table 3. Whiskers are set to 1.5 times the interquartile range and the orange bar indicates the arithmetic mean. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reaction time at 290 °C in NaOH (aq) were directly analyzed (i.e. without neutralization). Valenzuela Olarte commented on several general trends relating to HBCD treatment, namely [91]:

a) an increase in "oxidized" functional groups ($\delta_{13C} > 168$ ppm),
b) a reduction in aromatic functionality bearing methoxy groups ($\delta_{13C} = 144$–162 ppm),
c) a reduction in C-2 and C-6 syringyl groups (ca. $\delta_{13C} = 110$ ppm, relevant for hardwoods),
d) a decrease in the methoxyl group content in general ($\delta_{13C} = 56$ ppm) and
e) the appearance of aliphatic-related groups ($\delta_{13C} < 50$ ppm).

The differences between the spectra of 15 and 60 min retention time were small, i.e. the reaction is considered complete after 15 min, although heat-up time should also be taken into account.

Mahmood et al. have employed ATR FT-IR to characterize the transformation of lignin during HBCD processing and the associated products [90]. Here, the original KL was compared with acetone dissolvable products (referred to in that report as depolymerized lignin). Regarding further details on spectral band assignments in the FT-IR analysis of lignin the reader is also referred to the work of Lupoi et al., where also other analytical techniques are reviewed [23]. The reported work of Mahmood et al. indicated the spectral wavenumber range of
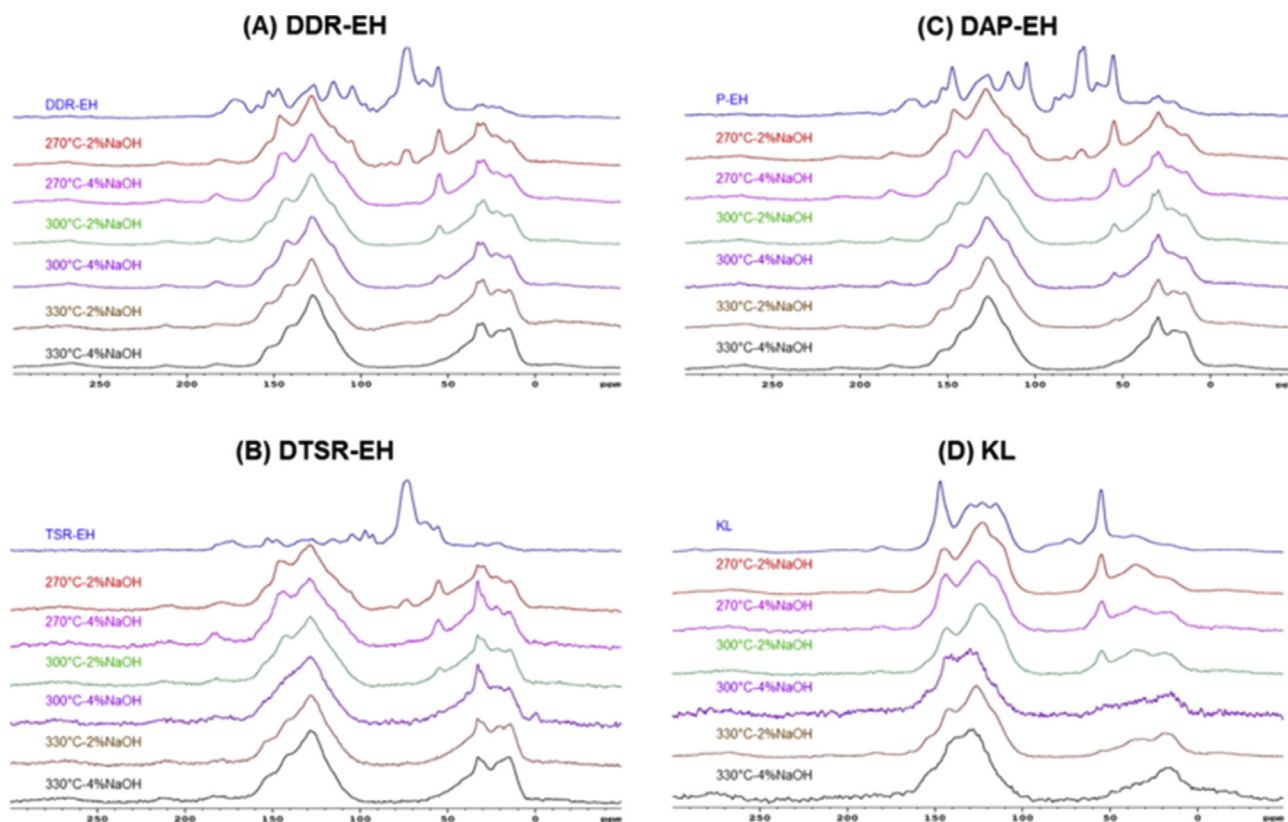
Table 3
Mass balance and major monomeric compounds of the reactions in basic environment given in Table 1.

Source	conditions	Mass Balance			Major Oil Components		Comments
		solid	liquid	gas			
#1	290 °C, 5 wt.% NaOH, 10 wt.% Kraft lignin, 23 min	65	20	15	yield of monomers catechol 4-methylcatechol 3-methylcatechol	 1.6 0.3 0.3	gas phase by difference yield probably refers to total lignin
#2	300 °C, 4 wt.% NaOH, 5 wt.% acetosolv lignin, 80 min	35	18	1	percentage of total oil catechol 4-methylcatechol 3-methylcatechol	 6.25 5.72 3.30	incomplete mass balance
#3	300 °C, 4 wt.% NaOH, 10 wt.% Kraft lignin, 40 min	61	23	4.7	percentage of GC peaks catechol 4-ethylcatechol 4-methylcatechol	 26.2 16.0 11.2	4-methyl-4-penten-2-one 4-methyl-3-penten-2-one 4-hydroxy-4-methyl-2-pentanone found in aqueous phase, probably derivatized from acetone
#4	300 °C, 5 wt.% NaOH, 10 wt.% softwood lignin, 45 min	70.3	5.5	n/d	percentage of GC peaks guaiacol 1,2-Dimethoxybenz. Acetovanillone	 52 15 9	
#5	300 °C, 5.5 wt.% NaOH, 20 wt.% softwood Kraft lignin, 60 min	93	7	n/d	n/d		the acetone dissolvable lignin is included in the solids fraction
#6	290 °C, 10 wt.% NaOH, organosolv lignin, 15 min	no mass balance			percentage of GC peaks catechol 4-methylcatechol guaiacol	 ~65 ~15 ~15	
#7	300 °C, 4 wt.% NaOH, 10 wt.% organosolv lignin (probably hardwood), 8 min	80.2	19.2	n/d	percentage of total oil syringol guaiacol 4-methylsyringol	 12 5 2	
#8	300 °C, 3 wt.% NaOH, hardwood organosolv lignin, 10 min	+80	10	n/d	percentage of oil syringol der. guaiacol der. catechol der.	 25.0 16.4 9.1	the oil composition is given as derivatives (der.) of the indicated types the yield of tar is not specifically indicated in the work and estimated from a diagram
#9	330 °C, 1 wt.% NaOH, 10 wt.% hardwood organosolv lignin, 60 min with addition of 3.8 wt.% of CaO only a 60 min reaction was done with quantification of the low pH aqueous phase	60	23	n/d			only 83% mass balance closed -> volatiles and gaseous products assumed he reactions concentrate on the ether soluble fraction and were also, in a previous study, done in CH_3CH_2OH and CH_3OH as solvent (see [80])
#10	300 °C, 4 wt.% NaOH, 5 wt.% hardwood organosolv (olive tree pruning), 40 min	50	20	n/d	percentage of total oil catechol 4-methylcatechol guaiacol	 10.2 5.2 1.2	70 % mass balance, no further indication towards the losses

Fig. 8. Solid-state ^{13}C NMR spectra of HBCD solid residues under six different conditions from the four substrates investigated by Katahira et al.; – (EH = Enzymatic Hydrolysis) – Deacetylated Corn Stover/Disk Refined/EH residue [DDR-EH], Deacetylated Corn Stover/Twin Screw Refined/EH residue [DTSR-EH], Dilute-acid Pretreated Corn Stover/EH residue [DAP-EH] and Kraft Lignin (KL). Reproduced with permission from Ref. [29].

1060–1160 cm^{-1} was sensitive to the HBCD treatment applied, showing a relative decrease in ether bond associated bands after the reaction. Lupoi et al. reported that various C–H in-plane deformations and C–H stretching bands for guaiacyl and syringyl units are to be found in this region [23]. Using Attenuate Total Reflectance (ATR) FT-IR for the analysis of the solid residue of a lignin process is convenient and seems promising when correlating the data to a 2D heteronuclear single quantum coherence spectroscopy (HSQC) NMR spectrum. Relative quantification *via* 2D HSQC NMR spectroscopy requires high signal to noise ratios and thus long machine run times, while providing unsurpassed spectral information on the compounds [22]. The relative quantity of C–H bonds for guaiacyl units at positions 2,5 and 6 gives information on the extent of alkylation and/or condensation of the lignin moieties. These can be found at (δ_{13C} = 110–125/δ_{1H} = 6.3–7.2) [22,102], These information can be correlated in a before-after analysis with data from ATR FT-IR. It would be interesting to see if the aromatic C–H in-plane deformations (1035, 1050, 1127, 1142 cm^{-1}) [23], and aryl ring breathing modes (1252, 1270, 1330 cm^{-1}) [23], show a comparable behavior (i.e. if they are shifted in position and/or are more or less intense).

4.3. The "oily" organic phase

The extract recovered from the low pH aqueous phase product of lignin HBCD (i.e. after solvent evaporation) is commonly referred to as the oil phase. Besides being dissolvable in low pH aqueous solutions, it is typically also a highly viscous liquid and totally dissolvable in polar organic solvents including CH$_3$OH, CH$_3$CH$_2$OH, acetone, or ethyl acetate. The analysis of this oil product is typically achieved via GC–MS (qualitative) and GC-FID (quantitative) (Table 2 and Table 3). The amount of the GC detectable compounds is often provided as yield of oil (i.e. when the compounds have been quantitatively calibrated)

[28,58,92,93], or as a percentage of the total GC peaks [30,31,91]. Schmiedl et al. were able to differentiate the composition of the oil based on the relative composition of syringyl, guaiacyl, and other hydroxylated compounds (i.e. based on a calibration with the respective compounds) [92]. Based on this work, it can be assumed that *ca.* 50 wt. % of the oil phase is GC detectable, although this value will vary based on the selection of extraction solvent (e.g. polarity).

Typically the main constituents of the oil are catechol and its derivatives (Fig. 9) (catechol, 3- and 4-methyl-catechol; Table 1; Entries #1–3, #6, #10), syringol or guaiacol (Table 1; Entries #7, #8). Lavoie et al. have reported that guaiacol and 1,2-dimethoxybenzene are the primary components, but the origin of the latter is not clear, since
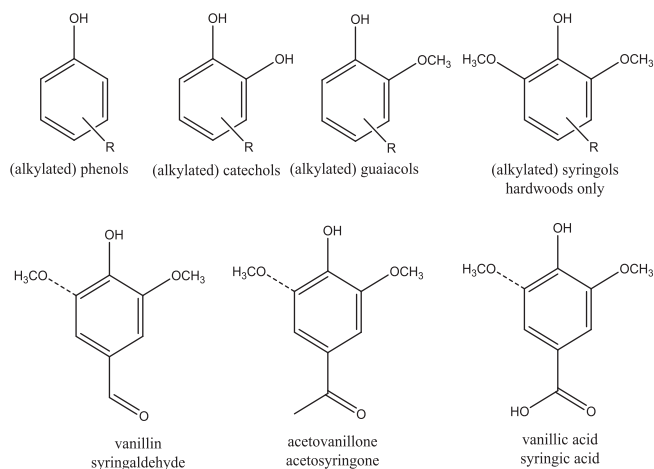

Fig. 9. Main monomeric compounds from base catalyzed hydrothermal depolymerization of technical lignins in aqueous phase.

methylation of hydroxyl groups does not occur in other reactions [31]. Catechol concentration has been shown to increase over retention time and at increased temperatures, whilst the concentration of guaiacol and syringol decreases (*NB: the latter is only relevant when hardwood-derived lignin is used*). The concentration of vanillin and acetovanillone is a lot lower than that of catechol or guaiacol, and only marginally influenced by retention time or temperature. The catechol concentration has also been shown to increase with increasing temperature at constant retention time (Table 1; Entries #1, #3, #4, #6, #8).

As a general rule catechol concentration is typically proportional to retention time. Katahira et al. experienced a maximum in catechol concentration at 300 °C for lignin derived from deacetylated/disk-refined/enzymatic hydrolysis process (which had initially a 33% sugar and 50% lignin Content) [30]. Valenzuela Olarte likewise reported that a maximum production was observed with a reaction temperature of 290 °C [91]. In this report the investigated temperatures were separated by large intervals (i.e. 160, 290, and 350 °C) and a long (60 min) retention time was chosen. Reported investigations relating to temperature dependence and values associated with specific compounds detected have been summarized (Table 1; Entries #3, #4, #6). These reports all show that alkylated catechols do not decrease, whilst guaiacol and alkylated guaiacols increase at the beginning, passing through a maximum, and subsequently decrease. Roberts et al. provide a very high time and temperature resolution for reactions conducted on hardwood lignin [58]. With the use of a small continuous reactor Roberts et al. were able to map very short retention times (2.5–15 min), deriving insight into the product distribution at the very beginning of the reaction. It was observed that after 15 min at 300 °C, in 2 wt.% NaOH (aq) with 5 wt.% organosolv hardwood lignin, the concentration of nearly all detected monomers is zero. Syringol is observed to reduce in concentration from 25% after 2.5 min over to < 10% after 10 min and to roughly zero after 15 min [58].

These findings are in accordance with Miller et al., in the reported study on a model syringol compound, where syringol is proposed to polymerize under the applied basic hydrothermal conditions [78]. In this context, it is important to consider the relationship of temperature, reaction rate (i.e. ratio of reaction rates (k_2/k_1)) and activation energy (E_A). Funaoka and Abe have previously reported that the E_A for the demethylation of guaiacol to catechol (*via* a nucleus exchange mechanism, reaction with boron trifluoride and excess of phenol), is *ca.* 126 kJ/mol [103]. Assuming a comparable E_A under basic conditions an increase of temperature from 300 to 320 °C would represent an increase in the rate constant by 2.5. An increase from 250 to 300 °C or 300 to 350 °C leads to an increase in rate constant roughly by a factor of 15, and 165 to 290 °C (Entry #6; Table 1) gives a factor of 2500. This is reflected by the product distribution reported by Valenzuela Olarte, which is very different at the two applied temperatures. These findings do not play a role when these reactions proceed significantly faster than the rate determining step of the whole system, but provide insight into the relationship between temperature change and increasing retention time.

Concerning the formation of the solid or residual phase, it appears based on the reported literature, that reactions of the forming monomeric phase initiates with "peeling off" of vanillin and acetovanillone (and derivatives) from the lignin backbone, which are then converted to syringol (i.e. for hardwood lignin-based processes) and guaiacol moieties. The reaction then proceeds *via* further polymerization (i.e. for syringols) or further degradation reactions to produce catechol and associated derivatives. Interestingly, the alkylated versions of catechol are rather stable, while eventually the catechol disappears (e.g. transformed to either alkylated derivatives or polymerized oligomeric compounds as described by Roberts et al.) [58]. Since the reaction mixture contains the aforementioned compounds in different concentrations (e.g. depending on processing, lignin source, *etc.*), but also lots of di-, tri-, and oligomeric substances which can serve as reaction partners, it is very difficult to derive one specific reaction pathway.

Although reports concerning the use of model compounds in this context can provide further insight they have to be interpreted carefully [21].

4.4. Gas phase products

In many reports on the HBCD of lignin, the gas phase is often not detected or analyzed (Table 3). However, regarding the overall process dynamics and ultimately the development of a large-scale process, it is an important consideration (e.g. regarding heat and mass flows). Beauchet et al. determined the gas phase by difference giving values between 15 and 25 wt.% [89]. Since they used a continuous reactor and did not include any coke (i.e. non-dissolvable components) in their mass balance, the gas phase contribution may include some contribution from coke. The measured amounts of gas were found to be stable in temperature range of 270–290 °C, followed by a significant increase upon increasing to 315 °C [89]. Erdocia et al. sampled the gas phase into a latex rubber inflatable device and measured it gravimetrically [28]. The amount was calculated as *ca.* 1 wt.% for all three of the investigated organosolv lignins at 300 °C and 80 min retention time. Since a temperature dependent investigation was not performed, the influence of a temperature increase cannot be determined.

In their report, Katahira et al. determined the gas phase gravimetrically after the reaction, weighing the reactor before and after releasing the gas, demonstrating an increase in gas phase contribution with increasing temperature [30]. The amounts of gas varied between 3.0 wt.% at 270 °C with a 2 wt.% NaOH (aq) and 9.3 wt.% at 330 °C with a 4 wt.% NaOH (aq) solution. The gas phase was not analyzed regarding its composition, but it was stated that probably CO_2 is generated which then reacts with the NaOH in solution to Na_2CO_3. CO_2 is then released upon acidification with HCl (aq). Schmiedl et al.et al. have reported that during the process of HBCD, CO and CO_2 are formed [92]. Yuan et al. report < 1 wt.% products are in the gas phase, as analyzed *via* GC-TCD, with this 1 wt.% composed of mainly CO_2 and H_2S [104].

5. Conclusions

Lignin, a major constituent of lignocellulose, is produced in industrially relevant amounts during pulp and paper processing. It is expected also to increase in availability given that it is a significant side product of 2nd generation biofuel production. Therefore lignin utilization will be critical with regard to the rapid and economically attractive roll out of integrated Biorefineries. When aiming at the implementation of a conversion process for precipitated lignin into a Kraft mill, it has been shown that it is advantageous to use NaOH (aq) regarding the base catalyst and dissolution agent. Reports indicate that a purely aqueous process generates comparable results, hinting at a thermally controlled hydrolytic reaction pathway [81,105], the ability to dissolve lignin offers advantages regarding reactor design and scalability. Through HBCD a low molecular weight fraction consisting of monomers, dimers, and some trimers can be produced, leading to maximum yields of 20 wt.%. The remaining 80 wt.% must valorized to render the complete approach economically feasible. It is difficult to define the optimal process conditions in terms of NaOH/lignin ratio, temperature, and retention time, since this depends strongly on the initial feed composition. The ratio of NaOH to lignin is known to be a critical factor influencing the extent of lignin conversion. The maximum lignin decomposition was reported at a NaOH:lignin mole ratio of 1.5–2 [76,78]. Additional reported research has focused further on process optimization with regard to monomer yield, typically employing temperatures between 250 and 300 °C, a short retention time (15 min) and, to some extent, the usage of capping agents preventing re-polymerization. The latter is problematic, since the consumption of these compounds can easily make the process uneconomical and may require further chemistry/processing to recover the employed agents unless

they themselves are incorporated into the recovered product (e.g. boron from boric acid). Furthermore, the low molecular weight oily organic phase is still relatively heterogeneous, while its composition can be partially driven towards catechol and alkylated catechol content through the use of higher reaction temperatures and longer retention times (300 °C, 30 min). However, this has been reported to lead to extensive repolymerisation and associated molecular weight changes. Therefore, the characterization of the solid residue is very important and has been approach through the use of a variety of analytical techniques. In this context, the use of 2D NMR techniques (e.g. HSQC) has proven to be useful when employed and cross correlated with other techniques (e.g. FT-IR, XPS etc.).

Finally, regarding complete lignin utilization, a potential application for the solid residue has to be found. Criteria for potential products have to be determined and the process parameters have to be optimized with regard to the highest value fraction of the products. Alternatively, the usage as a feed for an integrated gasification combined cycle (IGCC) has been proposed with carbon capture generating electricity and CO_2 [106–110,112]. Taking into account precipitation processes, Tomani has indicated that the main operating costs for the CO_2-based LignoBoost® process stem from the CO_2 acquisition [25]. With the aim of producing an aromatic source for the chemical industry, a biomass separation process other than the Kraft process should be considered. The high amount of C–C bonds within the Kraft lignin and their high bond dissociation energies would make it quite energy intensive from a thermodynamic point of view [21].

Its high-energy density and intrinsic aromatic character, lignin is in general a suitable renewable feedstock for Biorefineries to produce fuels, value-added chemicals, and functional materials. The most attractive and yet most challenging avenue for technical lignin valorization is the production of high-value chemicals, as a renewable route and alternative to Benzene, Toluene and Xylene (BTX) and phenol production. It is hoped with the further development of technologies currently under consideration (e.g. BioRizon – https://www.biorizon.eu/), the outlook for the valorization of lignin in general but in particular technical lignin is a positive one and will assist the chemical industry in ultimately sourcing aromatic feedstocks from renewable, sustainable sources. However, the selective conversion of technical lignin (and lignin in general) to desirable value-added products will, as for the current chemical industry, depend on catalysis. In this regard, challenges exist regarding the application of HBCD approaches to efficiently producing lignin-derived monomers. The main challenge is the tendency of intermediates/products to rapidly undergo (re)polymerization and/or condensation. It has been discussed that the selection of suitable capping agents, solvents *etc*. may assist in this endeavor, whilst pre-modification of technical lignin (e.g. through selective oxidation of C_αH-OH to C_α = O in β-O-4 linkages and reduction in bond dissociation energy) [110] may open scope for lower temperature processing, the application of heterogeneous catalysts and improved products yields.

Acknowledgments

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