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Process and product analysis of CO2 precipitated Kraft lignin

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AFFIDAVIT

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Abstract

In Austria, every year nearly 3 million tonnes of lignin, which is the second-most abundant biopolymer after cellulose, are burned in the recovery boilers of Kraft pulping mills. However, isolated lignin presents a promising raw material for sustainable production of value-added products like adhesives, stabilizers or even carbon fibres, while the extraction of lignin from black liquor reduces the often very high load on the chemical recovery boilers of the pulp mills. Acid precipitation with CO_2 as acidifier is a convenient way for lignin isolation from Kraft black liquor. In order to determine the ideal process parameters for precipitation of lignin, a literature study focussing on the state of the art processes currently applied on an industrial scale was performed. Precipitation in lab-scale using a stirred tank reactor was done based on published process conditions. Furthermore, a precipitation reactor in pilot scale was operated under similar conditions to evaluate the precipitation yield, the influence of CO_2 content in the acidifying gas and the effect of precipitation temperature. At the comparably high precipitation pH of 10-10.5 still up to 36 % of the total lignin could be precipitated from the feed black liquor. The filtration properties of the resulting lignin slurry were generally decent, the use of dilute CO_2 instead of pure gas led to a slightly increased filtration resistance in the range of $4 \cdot 10^{12}$ m^{-2} which still is considered as easily filterable.

For characterization of feed black liquor, the acid consumption as well as the buffer capacity of lignin phenolic OH-groups were investigated with titration experiments. Titration was carried out at varying temperatures, revealing the strong influence of the temperature on the pH and the pK_a values of black liquor and the constituents thereof.

Kurzfassung

Jedes Jahr fallen bei der Zellstoffkochung knapp 3 Mio. Tonnen Kraft-Lignin an, welches im Recovery-Boiler als Brennstoff verwendet wird, nach Zellulose ist es das zweithäufigste Biopolymer. Aufgrund des hohen Vorkommens kann dem Lignin in einer biobasierten Zukunft daher eine tragende zukommen, die potentiellen Anwendungen von Kraft-Lignin reichen von Klebstoffen und Stabilisatoren bis hin zu Karbonfasern. Die Ligninisolierung aus der Schwarzlauge bringt weiters eine Entlastung des Recovery Boiler mit sich. Es wurde eine Literaturstudie mit dem Fokus auf die derzeitigen Stand-der-Technik Verfahren durchgeführt und basierend auf den Ergebnissen wurden Versuche im Laborreaktor durchgeführt. Unter vergleichbaren Bedingungen wurde ein Reaktor im Technikums-Maßstab betrieben, um den Einfluss der CO_2-Konzentration im Fällungsgas und der Fällungstemperatur auf die Ligninausbeute und die Filtrierbarkeit zu untersuchen. Bei einem vergleichsweise hohen Fällungs-pH von 10-10,5 konnten bis zu 36 % des Gesamtlignins aus der Schwarzlauge ausgefällt werden. Die Filtrationseigenschaften der resultierenden Ligninsuspension waren gut, die Verwendung von verdünntem CO_2 anstelle von reinem CO_2 führte zu einem etwas höheren Filterwiderstand von $4 \cdot 10^{12}$ m^{-2}, was als einfach zu filterndes Material gilt.

Um die Schwarzlauge zu charakterisieren, wurden der Säureverbrauch und die Pufferkapazität der phenolischen OH-Gruppen von Lignin mithilfe von Titrationsexperimenten untersucht. Die Titration wurde bei verschiedenen Temperaturen durchgeführt, wodurch der Einfluss der Temperatur auf pH und pK_a von Schwarzlauge und ihren Inhaltsstoffen verdeutlicht wurde.

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1   Introduction

Throughout the world the public awareness towards the imminent danger associated with climate change has strongly increased during the last two decades [1]. The adverse consequences of climate change and the problem itself have been tackled on many different levels, where policy makers, researchers and organizations seek to mitigate emissions and slow global warming. However, other interests like economic profit or personal wellbeing are sometimes in opposition to such efforts [2]. Another factor driving the need for alternative ways of production and energy generation is the fast depletion of fossil fuels. The peak of conventional mineral oil production has likely been passed sometime during the last decade, and complete depletion is estimated to be within the next 30-70 years [3]. Although there are certain unconventional fossil fuel reserves whose extraction could considerably prolong the time until depletion, the need for alternative, sustainable sources of raw materials and energy is evident [4].

Considering the current trajectory of global greenhouse gas emissions, it is unlikely that the strived goal to limit global warming to less than two degrees can still be achieved [2]. All the more urgent is the need to develop sustainable production technologies based on renewable resources instead of fossil fuels. In Austria, the pulp and paper industry is one of the biggest sectors of bio-industry with more than 30 sites throughout the nation [5]. Already being a so-called biorefinery which produces besides pulp also many additional products like tall oil, turpentine, acetic acid and energy from the renewable resource wood, it is an obvious candidate for further progress towards integrated biorefinery concepts and downcycle raw material utilization of resources [6].
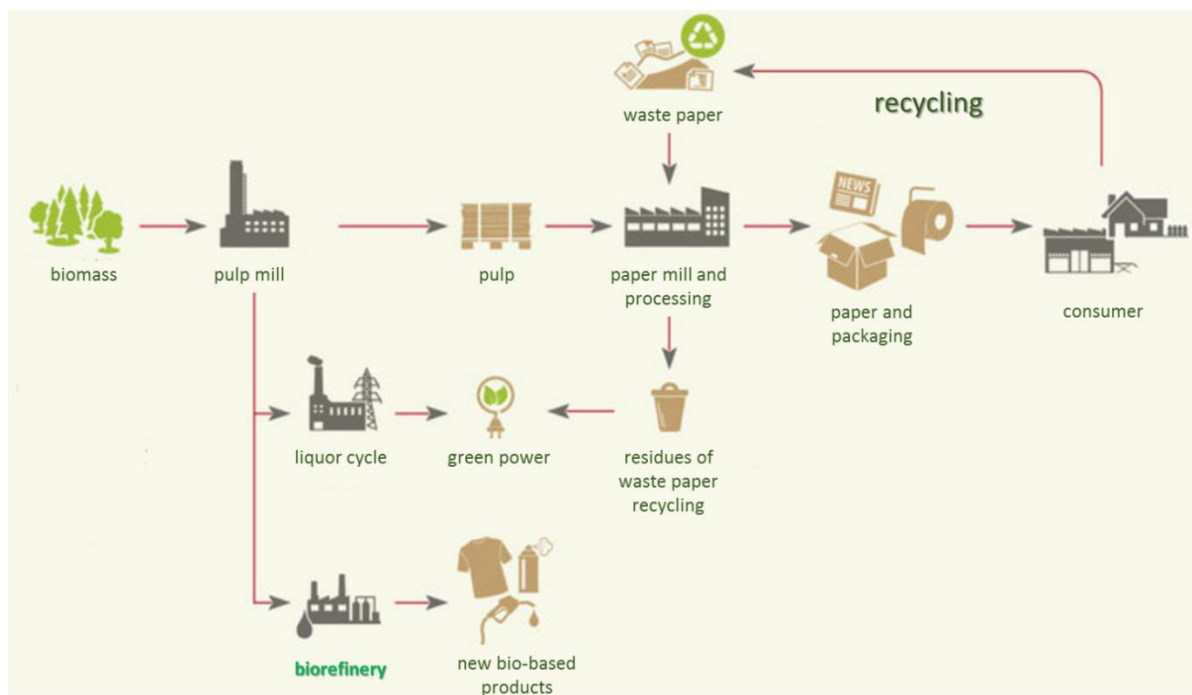

Figure 1. The Austrian pulp and paper industry and associated product and material fluxes. Adapted from [7].

Figure 1 shows the flux and circulation of raw materials and products associated with the pulp and paper industry. If the pulp mill utilizes the Kraft process, the chemical recovery stream of black liquor (BL) contains a large amount of the biopolymer lignin, which constitutes for about 30 % of wood biomass [8]. Currently lignin is usually burned to recover process chemicals and generate energy. Due to the high volume and its potential as future bulk chemical, isolation of lignin is a promising option for pulp and paper mills to take a step further towards sustainable production of value-added products from wood.

1.1   Objectives

The present thesis is conducted as part of the "lignin isolation" work package of the FLIPPR[2] project, which is a joint effort of Austrian scientists and the local pulp and paper industry. One of the project goals is the on-site integration of a lignin isolation process and the development of analytical and processing procedures for the isolated lignin product.

The investigation of various aspects of lignin isolation from Kraft black liquor is the main objective of the present work. A thorough literature review focussing on the state of the art processes for lignin precipitation by acidification of black liquor gives a solid basis for the design and evaluation of a new lignin precipitation process. Such a new process needs to give a similar performance as state of the art processes, the present work is concerned especially with the filterability of the lignin product. All the experiments are carried out with Kraft black liquor received from a local pulp and paper mill.

During lab-scale experiments, a feasible range for various process parameters is identified and a lignin mass balance is calculated from the experimental data. Based on these preliminary experiments a pilot scale precipitation process is designed.

Balancing calculations based on lignin mass in the feed and in the product streams are performed with the data obtained from the pilot scale precipitation experiments. The lignin slurry received from the precipitation experiments is filtered and the specific filter cake resistance is determined experimentally. The correlation between the resulting resistances and the varied process conditions is evaluated.

The feed black liquor is characterized with titration experiments. From the resulting titration curves, the pK_a of the dissolved lignin is estimated. Furthermore, the resulting data is used to determine the approximate amount of phenolic OH-groups of the lignin molecules. The difference in neutralization course depending on the titration temperature and the corresponding change of lignin pK_a is investigated too.

The solubility of lignin precipitated with the new process is estimated. Based on the results, the feasibility of membrane processes like ultrafiltration can be evaluated.

1.2 Kraft process

Globally, 77 % of pulp is produced via chemical pulping processes. The so-called Kraft pulping process accounts for 95 % of this pulp, which renders it one of the most important bio-industry processes [9]. Kraft pulp is characterized by a very strong pulp fibre product, a characteristic mirrored by the process name "Kraft", which is the German word for strength. In comparison to that, a low pulp yield, costly and extensive equipment and the formation of odorous sulphur compounds are the major disadvantages of this process [10].

The Kraft process has a very advanced and well-established recovery process cycle for recycling of process chemicals. The liquor cycle is depicted in the flow chart in Figure 2.
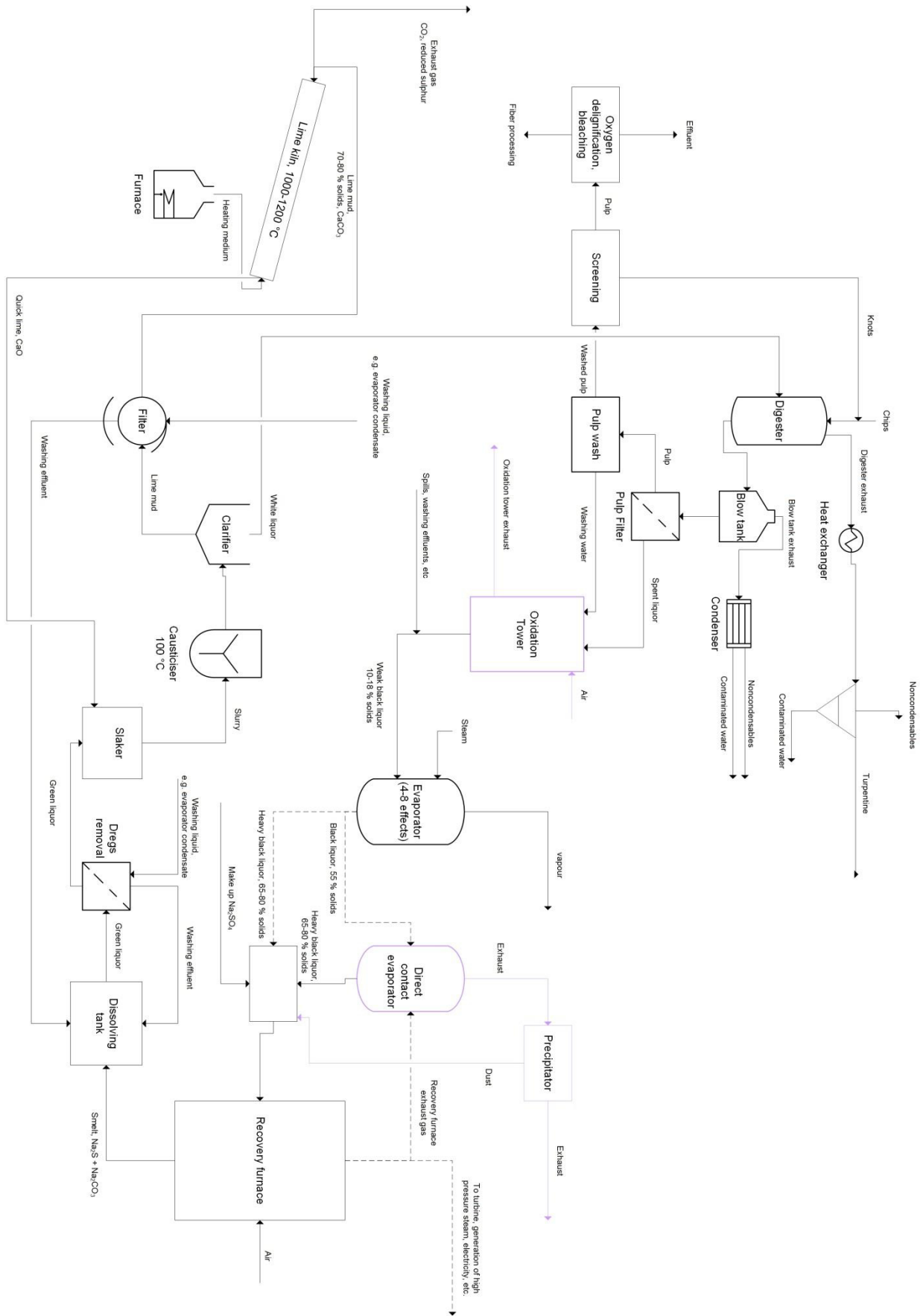
Figure 2. Detailed flow chart of the Kraft process' chemical recovery cycle. Process steps in light purple are optional.

In the digester the wood chips and white liquor containing the cooking chemicals Na_2S and NaOH are mixed and the pulp is cooked for 1-4 hours at 140-170 °C and increased pressure [9]. The cooking conditions differ from mill to mill and also depend on the type of wood used. During cooking non-cellulosic wood material is dissolved in the cooking liquor. The wood disintegrates when the cooked mixture is pumped to the blow tank where it is depressurized to atmospheric conditions [11]. Thereafter, the pulp is separated and washed by filtration. The resulting liquid fraction is called weak black liquor and contains 10-18 wt% solids [9]. For combustion in the recovery boiler this stream needs to be concentrated to a solids content of 60-80 % in the multiple effect evaporator, which usually comprises 4-8 units. The condensate can be used for example for pulp washing, bleaching or recausticising [9]. Throughout the evaporation, soap and tall oil is skimmed from the black liquor at one or more stages.

The black liquor with a final solid content of 60-80 % is called heavy black liquor, and is fed to the recovery boiler after addition of make-up chemicals (Na_2SO_4 and NaOH or Na_2CO_3). In the boiler, the liquor is burned with oxygen at approx. 1000 °C. The flue gas is then used for generation of hot steam in a heat exchanger before the dust is separated in e.g. an electrostatic precipitator. The corresponding CO_2 content is approx. 20 % [12]. The recovery boiler is one of the most expensive pieces of equipment in the mill and thus often the bottleneck for pulp production. If the load exceeds the maximum capacity, the exhaust gas contains contaminants like H_2S, SO_2 and NO_x [9], [13]. Therefore, a reduction of the boiler loading by extraction of lignin and thereby reduction of the heating value of black liquor, is an additional motivational factor for isolation of lignin at many mills. When around 30 % of lignin are extracted, the pulp production can in turn be increased by up to 23 %, without the necessity to install a bigger recovery boiler [14].

At the bottom of the recovery boiler, the cooking chemicals, called smelt, are extracted and dissolved in e.g. washing liquid to form green liquor. This liquor is then filtered to remove dregs and thereafter mixed with quicklime (CaO). During causticizing the mixture is heated to 100 °C and the sodium carbonate from the smelt is converted to sodium hydroxide according to Equation 1.

$$Na_2CO_3 \ + \ CaO \ + \ H_2O \rightarrow CaCO_3 \ + \ 2\,NaOH \qquad \text{Equation 1}$$
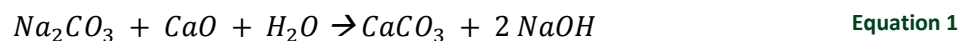
The solid $CaCO_3$ is then separated from the liquid fraction by clarification or filtration. In the lime kiln the lime mud is calcinated at 1000-1200 °C to form CaO again. The off-gas of the lime kiln contains up to 30 % of CO_2 [9]. The liquid fraction after caustization is called white liquor and is cycled back to the digester. With that, the recovery cycle is closed with very little loss of chemicals in the form of ash and off-gases.

1.3 Lignin

The lignin isolated from Kraft BL is different from native lignin as shown in Figure 3. Lignin is, after cellulose, the most abundant biopolymer and constitutes for around 20-30 % of wood biomass, depending on the species [15].
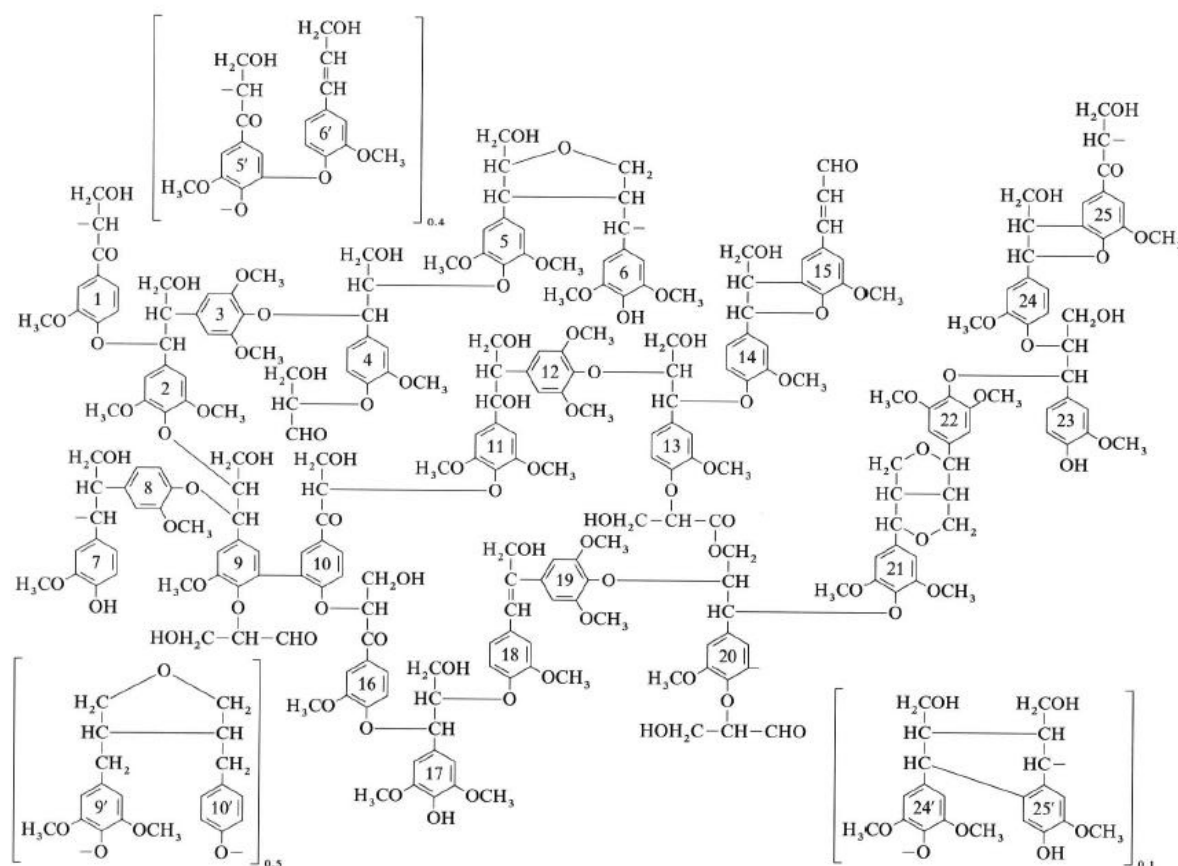

Figure 3. Exemplary constitutional scheme of native lignin from beech [16].

During Kraft pulping the lignin is fragmented under the harsh cooking conditions. The fragments, being more hydrophilic than native lignin, dissolve in the black liquor. Already native lignin is of varying structure and processing usually only increases the heterogeneity. The lignin structure is typically based on the phenylpropane units of p-hydroxyphenyl, guaiacyl and syringyl types [17]. A simplified moiety of lignin showing some typical functional groups is depicted in Figure 4.
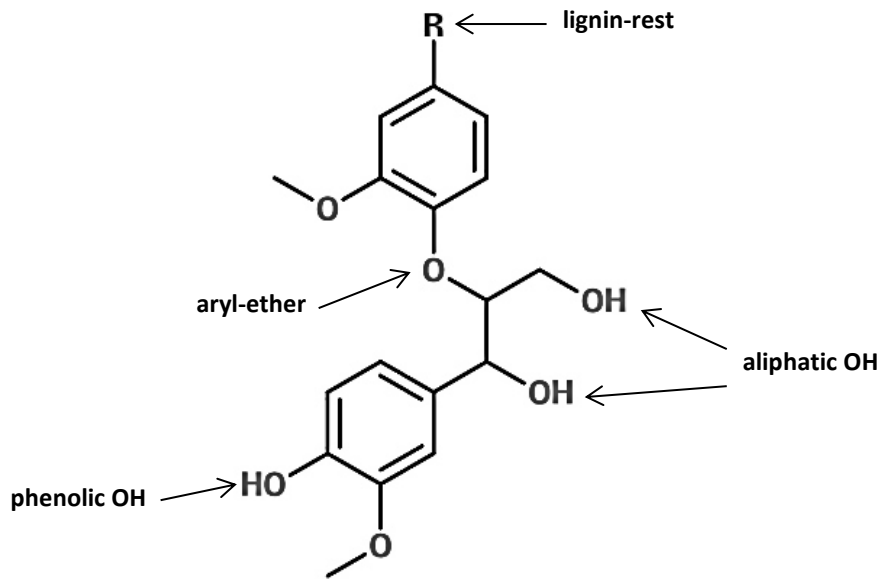
Figure 4. Schematic substructure showing the different functional groups of lignin. Adapted from [18].

Lignin fragmentation in the digester leads to formation of new phenolic hydroxyl groups (Ph-OH groups) by cleavage of aryl ether bonds [19]. Smaller lignin units are dissolving faster and the larger molecules only dissolve during the final delignification stages. Therefore, the properties of Kraft lignin can vary strongly with the cooking conditions. Furthermore, lignin liberated during Kraft cooking may be linked to carbohydrate units, forming lignin-carbohydrate complexes. The extend of such complexes in the black liquor again depends on the cooking conditions [20]. The same holds for the lignin molecular weight. Kraft lignin typically has an average molecular weight between 1100 and 6500 g·mol^{-1} [21].

Currently isolated lignin is used on-site as fuel in the lime kiln, but potential value-added products are vanillin, carbon fibres, phenolic resins and phenol derivatives as well as phenol, bitumen, cement and concrete additives, dispersants and binders [22].

2   Literature review: Kraft lignin isolation

Lignin extraction from Kraft black liquor can be done at several stages of the evaporation train. For some methods, the properties of weak black liquor with low solids content are more suited, for others the performance is best when intermediate black liquor is used. The remaining mother liquor, which is also called lignin-lean black liquor (LLBL) is preferably recycled to the evaporation train to assure the least possible impact on the recovery cycle.

The lignin content of Kraft black liquor depends on cooking conditions and wood species and lies in the range of 30 % of total solids (DS) [23]. In the literature several processes for extraction of at least part of that lignin are discussed: acid precipitation, membrane processes, electrolysis and solvent extraction.

2.1   Acid precipitation

2.1.1   Mechanism

Currently acid precipitation is the most advanced and industrially implemented technology for recovery of lignin from Kraft black liquor [24]. In black liquor, that usually has a pH around 13, the lignin molecules are supposed to be dissolved in a colloid-like form, with their negatively charged phenolic hydroxyl groups distributed evenly near the surface around a more hydrophobic core. The Ph-OH groups are weakly acidic, so their dissociation behaviour can be described, depending on H^+ concentration and hence pH of the solution, according to Equation 2.

$$Lignin - Ph - OH \leftrightarrow Lignin - Ph - O^- + H^+$$

Equation 2
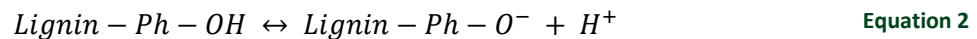
At high pH values and thus low H^+ concentrations, the negatively charged lignin molecules are associated with sodium counter-ions and remain stable in solution because of repulsive electrostatic forces. When the pH drops to the range of the pK_a of the Ph-OH groups, their degree of protonation increases with increasing H^+ concentrations and thus also the repulsive forces decrease. The attractive hydrophobic forces (e.g. van der Waals forces) increase and the lignin molecules partially precipitate out of the solution. The degree of precipitation depends on different factors, like pH, the lignin structure and the temperature as well as the ionic strength. With lower pH, the precipitation yield increases, while an increase of ionic strength also leads to enhanced precipitation yield and filtration properties. The lignin structure is depending on the functional groups and the molecular weight, which in turn depend on the biomass and the pulping conditions. [18]

Typically isolated lignin is further acidified well below the lignin pK_a, which lies in the range of 10. The low pH of 2-4 assures a complete protonation of sodium lignate to form hydrogen lignate, leading to an insoluble lignin product with low sodium content (and thus low ash content). Low sodium content

in a solid lignin fuel product is necessary to avoid problems with corrosion and ring formation in the combustion equipment. Furthermore the sodium washed out of the cake can be recycled to the liquor cycle which reduces the detrimental effect of lignin extraction on the Na/S balance and thus the make-up requirements of a pulp mill [25].

2.1.2   State of the art processes

Acid precipitation of lignin is usually performed using either carbon dioxide or sulphuric acid. While the pH can only be reduced to around pH 7 using CO_2, H_2SO_4 can be used to lower the pH to any desired value. The use of CO_2 is beneficial since it does not disrupt the Na/S balance of the pulp mill in cases where the lignin lean black liquor and/or the washing liquid is recycled to the liquor cycle [26]. A general scheme of the acid precipitation process is shown in Figure 5. Today there are three major processes for industrial scale acid precipitation, which are marketed as LignoBoost, LignoForce and SLRP (sequential liquid-lignin recovery and purification), respectively.
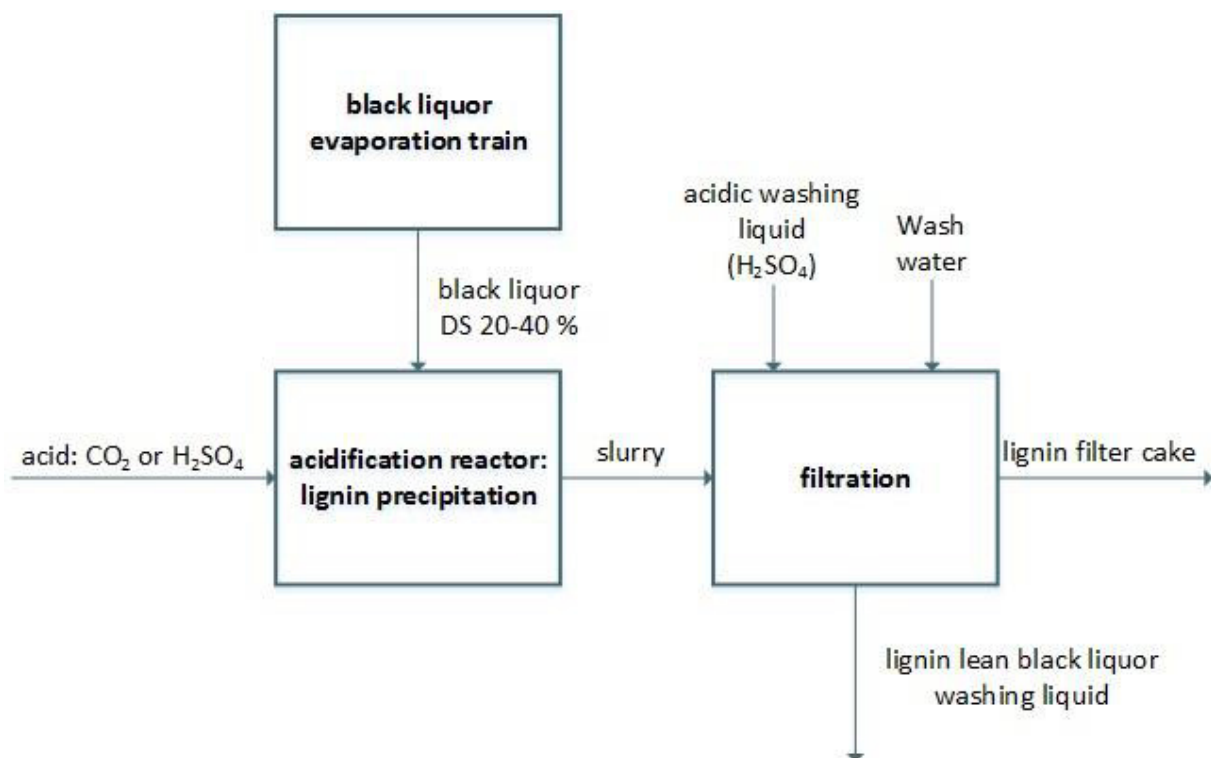

Figure 5. Schematic depiction of the general process for acid precipitation of lignin from Kraft black liquor.

2.1.2.1   LignoBoost

The LignoBoost process was developed during a project at Chalmers University of Technology (Gothenburg, Sweden) in cooperation with the Swedish research institute Innventia which was launched in 1996. Now the process is commercialized by Valmet Corporation of Finland and the first full scale industrial LignoBoost plant was Domtar's pulp mill in North Carolina (start of production in

2013), with a capacity of 25,000 tonnes of isolated Kraft lignin per year. In 2015 the second commercial LignoBoost plant was integrated in Stora Enso's Sunila mill in Finland producing 50,000 tonnes of lignin product annually. [18], [27]

A flow chart of the LignoBoost process is shown in Figure 6.
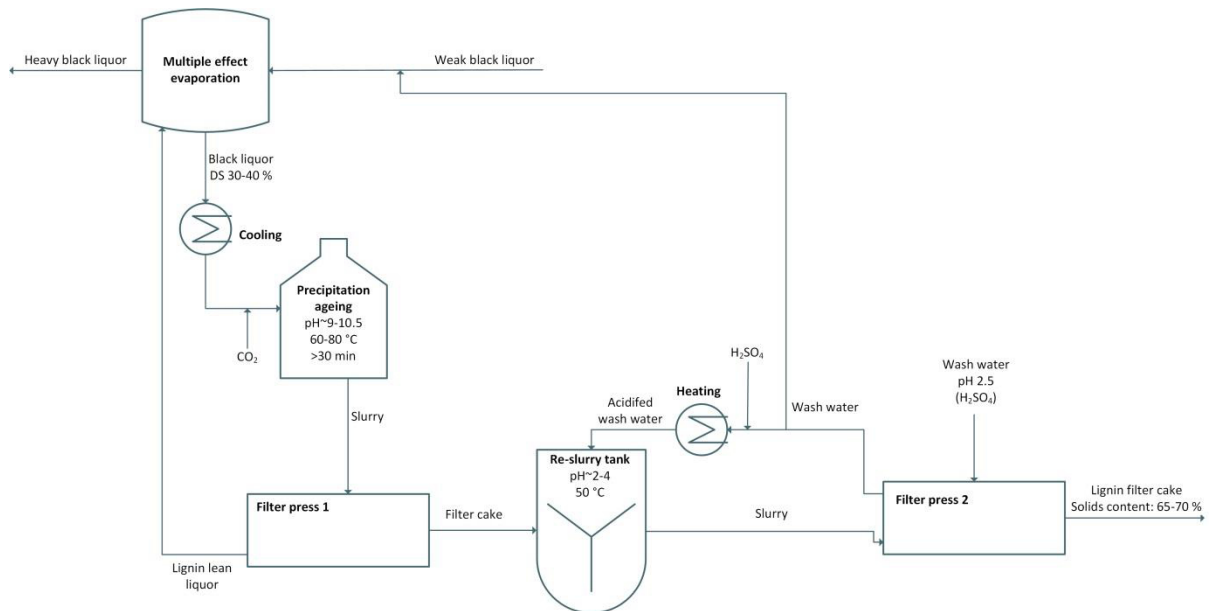
Figure 6. Detailed process scheme of the LignoBoost lignin isolation system.

Lignin precipitation

A black liquor stream with a solids content of typically 30-40 % is withdrawn at a suitable position from the evaporation train and cooled down to the precipitation temperature of 60-80 °C [18], [28]. Thereafter the acidifying agent is added to a final pH of preferably 9.0-10.5. The acid applied could e.g. be a mineral acid like H_2SO_4, but on an industrial scale it is preferred to use CO_2 instead since this does not disrupt the Na/S balance to the same extend and also gives the possibility to use certain off-gas streams of the pulp mill for acidification [29], [30]. If CO_2 is used for the acidification, the process can be carried out in a simple stirred tank equipped with a sparger for CO_2 introduction positioned below the stirrer [25], [28], [30]. The CO_2 demand for precipitation is reported to be 150-320 $kg \cdot t^{-1}$ of isolated lignin [31] .

In 2011 Björklund et.al. filed a patent application where they describe a two-step acidification procedure. In that process, the pH of BL is lowered with CO_2 by at least one pH unit until no more than 10 % of the lignin is precipitated. In a second acidification step, the BL is acidified to the final pH, which is preferable above pH 10, again using CO_2 as acidifying agent. This precipitation can be performed in two consecutive carbonizing towers, where the first one is designed to promote the maximum contact area between BL and CO_2, e.g. by use of random packings. The second precipitation tower where the majority of precipitation takes place is then designed without tight packings in order to prevent

blockage due to solid precipitate. Precipitation could also be performed in a single tower with two distinct zones enabling the two-step precipitation process. This patent also claims re-circulation of H_2S and CO_2 liberated in the second carbonization tower to the feed BL of the first precipitation stage [32]. In a similar patent granted to Metso Power Ab, Wimby et.al. describe a process similar to the one above, comprising an additional storage phase of 25-45 min after the first acidification stage, which seemingly reduces the filtration resistance of the lignin precipitate by 50 %. The reason for that is stated to be Ostwald ripening of lignin particles throughout this intermediate storage phase [33].

After acidification, the slurry is aged for typically 30-60 minutes in order to equilibrate the mixture and promote growth of lignin particles by agglomeration. Gentle stirring supports this ageing process. Wallmo and co-workers found that the filtration resistance of the slurry decreased upon ageing at 300 rpm and 60 °C. However, a higher mixing speed of 600 rpm led to increased filtration resistance, because the agglomeration that usually takes place during the ageing period was overlaid by an attrition effect caused by higher shear rates [30].

Precipitate isolation and purification

The lignin slurry is thereafter filtered using a suitable filtration device, most preferably a filter press. Thorough dewatering of the formed filter cake is very important, since the residual black liquor retained increases the amount of acid needed to further acidify the suspension formed in the following step. Dewatering can be promoted by application of pressure and blowing of air through the cake in order to displace the residual liquor [25].

After filtration the unwashed filter cake is re-dispersed in an acidic solution, where the pH and temperature are adjusted to be similar to that of the washing liquor used in the second washing step. This re-slurry stage is the main difference between the LignoBoost process and a conventional lignin precipitation process. In a conventional process, where the lignin cake is subjected to an acid wash step directly after filtration, significant problems regarding high filtration resistance and filter cake plugging are reported in the literature [25], [28]. These problems supposedly arise due to restructuring of the lignin precipitate throughout the washing process, caused by partial dissolution of lignin in the filter cake. Part of the precipitated lignin re-dissolves during the washing procedure when the ionic strength in the cake is already approaching the lower value of the acidic washing solution (pH 1.05 in that study) but the pH is still high [25]. The dissolved lignin can then re-precipitate in the filter medium and hence cause plugging thereof. In order to avoid high gradients of ionic strength and pH in the filter cake, the re-slurry step was incorporated into the LignoBoost process.

During the re-slurry step, the filter cake is suspended to solids concentration of around 15 %, preferably with acidic filtrate recycled from the subsequent washing step. The pH of the acidic solution is adjusted with H_2SO_4 so that the final pH in the slurry equals the pH of the (more dilute) washing liquid [34]. For that, typically a pH of 2-4 is chosen, leading to a pure lignin product suitable for industrial applications.

The necessary amount of sulphuric acid for pH adjustment depends on the precipitation pH and is reported to be approx. 120-255 kg·t^{-1} of lignin isolated [31].

After resuspension and pH adjustment, the slurry is gently stirred and equilibrated for 30-60 min. During this step, gaseous H_2S (and other totally reduced sulphur compounds) and CO_2 are formed due to the lower pH, which leads to protonation of the HS^- and HCO_3^-/CO_3^{2-} species [35]. These off-gases are not only strongly odorous, but might also cause foaming problems during the resuspension stage [25], [36]. The vent gases can then be collected and scrubbed with absorbent, e.g. white liquor in order to remove the odorous and toxic compounds from the exhaust gas [37].

Following the re-slurry step, the suspension is again filtered in a second filter press. The first acidic filtrate as well as the washing liquid can be recycled to the weak black liquor. The filter cake is washed with dilute sulphuric acid solution which comprises a lower ionic strength but the same pH as was adjusted during the re-slurry step [25], [38]. Öhman et.al. observed that lignin losses caused by re-dissolution due to low ionic strength in the washing liquid and problems with plugging of the filter cloth could be avoided by lowering the wash water pH to 2-3 [25].

If fresh water is used for washing of the second lignin filter cake, the H_2SO_4 demand to reach a pH of 2 is approx. 0.5 kg H_2SO_4/m³ of wash water, which is negligible compared to the amount required for re-suspension. The total necessary volume of wash water is reported to be 2-2.5 m³·t^{-1} of isolated lignin [31], [39].

The produced second lignin filter cake has a solids content of 65-70 % after pressing and blowing with air or another suitable gaseous stream [37]. The filter cake can then be further processed, e.g. by drying, pulverizing or pelletizing. The lignin produced with the LignoBoost process has a reported ash content of 0.2-1.4 % based on dry lignin product [31].

Recycle streams

The lignin lean liquor filtrate generated during the first filtration stage can be recycled either to the weak black liquor tank or to the evaporation train after the point where BL was withdrawn for lignin precipitation. The latter configuration avoids repeated withdrawal of BL where the lignin content had already been reduced by precipitation. The filtrate and washing liquid from the second filtration stage can be recycled to the weak black liquor, which causes a minor increase of evaporation load and steam demand for the evaporators [14]. It is advantageous to use at least part of the filtrate of the second filtration step in the resuspension stage in order to reduce the necessary amount of fresh liquid added to the process [40].

Instead of fresh sulfuric acid, acidic waste streams that are produced on-site could be used for the second acidification step. These streams could e.g. originate from a chlorine dioxide generation plant [33].

The purchase of fresh carbon dioxide is one of the major operation costs associated with lignin precipitation [30]. On-site there are two gaseous waste streams containing carbon dioxide, originating from the recovery boiler and from the lime kiln [12], [26]. Use of one of these flue gas streams for the first acidification can significantly reduce the operation costs of the lignin precipitation process. Lime kiln flue gas is usually proposed for this application since the carbon dioxide content is with 15-30 % higher than that of the recovery boiler flue gas [37]. The use of on-site flue gas for acidification is generally possible for all three processes discussed in this section. However, to the author's knowledge none of the industrial lignin isolation plants actually uses dilute CO_2 streams.

During the second acidification step, the slurry emits a gaseous stream consisting mainly of H_2S and CO_2. As already mentioned, these gases can be added to the feed BL stream prior to - or during - the first acidification step, in order to significantly reduce the necessary amount of acidifier [40]. Another possibility to use the produced H_2S would be conversion to SO_2 (and possibly to H_2SO_3 or H_2SO_4) prior to addition as acidifying agent [41].

2.1.2.2 LignoForce

The LignoForce process was developed by FPInnovations [42]. Commercialized by NORAM engineering, the first industrial pulp mill that implemented the LignoForce system is West Frasers pulp mill in Hinton, Canada in March 2016 [43]. The lignin extraction plant is designed for a lignin recovery rate of 30 t/day, which corresponds to an annual production of 10,000 tonnes of lignin product [44].

A depiction of the LignoForce process is shown in Figure 7.
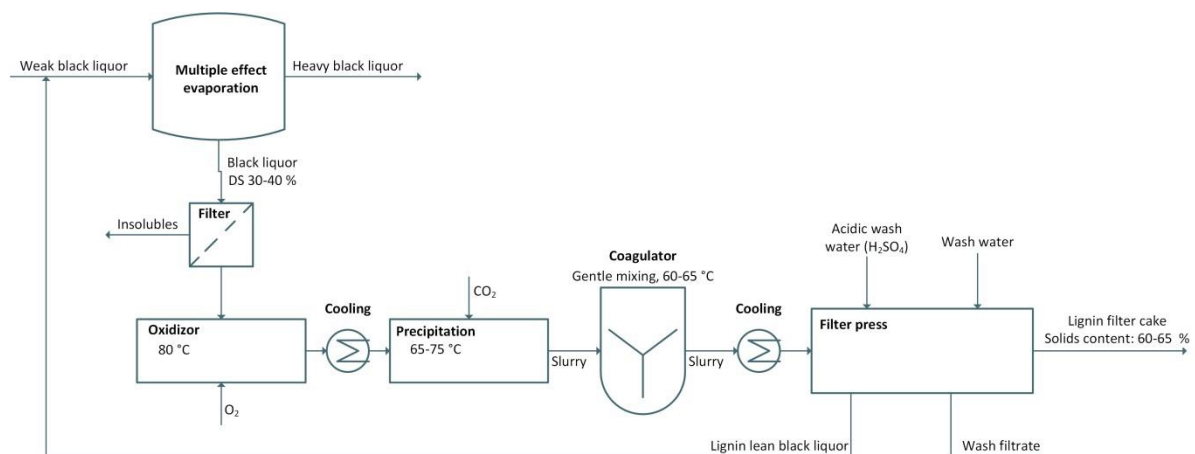
Figure 7. Detailed process scheme of the LignoForce lignin isolation system.

Oxidation step

The main characteristic of the LignoForce process is the implementation of a BL oxidation step prior to lignin precipitation. By that, various compounds in the BL are oxidized which leads to improved filtration properties and decreased liberation of toxic or odorous sulphur compounds.

Pure oxygen is added to the feed BL at a temperature of 80 °C until a residual sulphide content of 0-0.5 g·L^{-1} is reached [45]. Wels and coworkers reported an oxygen demand of approx. 210 kg O$_2$ per tonne of isolated lignin [46]. The following oxidation reactions might take place [45]:

$$2\ NaHS\ +\ 2\ O_2 \rightarrow Na_2S_2O_3\ +\ H_2O$$

$$Na_2S_2O_3\ +\ 2\ O_2\ +\ 2\ NaOH \rightarrow 2\ Na_2SO_4\ +\ H_2O$$
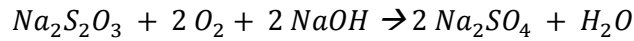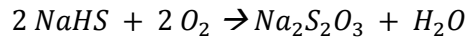
$$Totally\ reduced\ sulphur\ (TRS)\ compounds\ +\ O_2 \rightarrow non-volatile\ sulphur\ compounds$$

$$Sugars\ +\ O_2 \rightarrow sugar\ acids$$

The improved filtration properties of the lignin isolated from oxidized BL could possibly be partially attributed to the increase in ionic strength caused by the conversion of monovalent HS$^-$ to divalent SO$_4^{2-}$ ions. A higher degree of oxidation could be achieved by an increase of oxidation temperature and/or prolonged oxidation time. Thereupon additional oxidation reactions like the oxidation of hemicelluloses to the corresponding isosaccharinic acids or even shorter organic acids can take place. The content of hemicelluloses could also be reduced by prolonged incubation of oxidized BL at increased temperature, again leading to generation of saccharinic acids and a presumed improvement of filtration properties. The acidic compounds formed during the oxidation step lead to a significant decrease of pH value. [47]

A drawback of the oxidation is that - to a certain extent - lignin is expected to be oxidized to carboxylated lignin. This lignin derivative is mostly soluble at pH 4-10 and would thus not be precipitated during the acidification step.

Precipitation, filtration and washing

The precipitation is carried out at a constant temperature of 70-75 °C with carbon dioxide until a pH of 9.5-10 is reached. This corresponds to a CO$_2$ demand of 200-400 kg per tonne lignin isolated [42]. This step is followed by an ageing/coagulation step under gentle mixing at 60-65 °C in order to produce more easily filterable lignin particles. This slurry is then filtered in an ordinary filter press followed by washing with sulphuric acid and water in the filter press. The lignin filter cake is pressed and air-blown in order to increase the solids content. The final lignin product has a solids content of approx. 65 % [45]. The filtration rate of lignin precipitated from oxidized BL is 1.25-2.5 times higher than that of the corresponding unoxidized liquor [42]. The amount of TRS compounds produced is considerably reduced by the oxidation procedure. Kouisni and co-workers reported emissions of volatile sulphur compounds of 2.2 g·kg^{-1} lignin for the oxidised BL compared to 75.5 g·kg^{-1} lignin for untreated BL (expressed on an S basis). Furthermore, the lignin product formed lower amounts of volatile TRS

compounds upon heat treatment compared to conventionally produced lignin. This is beneficial in cases where lignin is further processed under increased temperature [45].

The oxidation reaction leads to formation of e.g. thiosulphate that can then further react to form volatile SO_2 at pH levels below pH 4. For oxidized BL, SO_2 emissions of approx. 1 g·kg^{-1} lignin where detected during the second acid wash, while there was no SO_2 formed during lignin isolation from unoxidized liquor. Under industrial conditions these amounts are expected to be negligibly low and furthermore be vented to the non-condensable gas treatment system of the pulp mill [35], [45].

The ash content of the final lignin product depends on the amount of washing water used. In one publication the introduction of 10-15 m³ of water/tonne of lignin led to an ash content of 0.07-0.18 % [47]. In industrial praxis, the applied amount of washing water was stated to be 4-5 m³·t^{-1} lignin [24].

2.1.2.3   Sequential liquid-lignin recovery and purification process: SLRP

The first provisional patent application for the SLRP™ process was filed in 2009 by Michael Lake and John Blackburn. Together, they founded the Liquid Lignin Company, which "develops and commercializes new lignin-based technologies" [48]. The company currently tries to find investors and industry partners for implementation of the SLRP process and associated products.

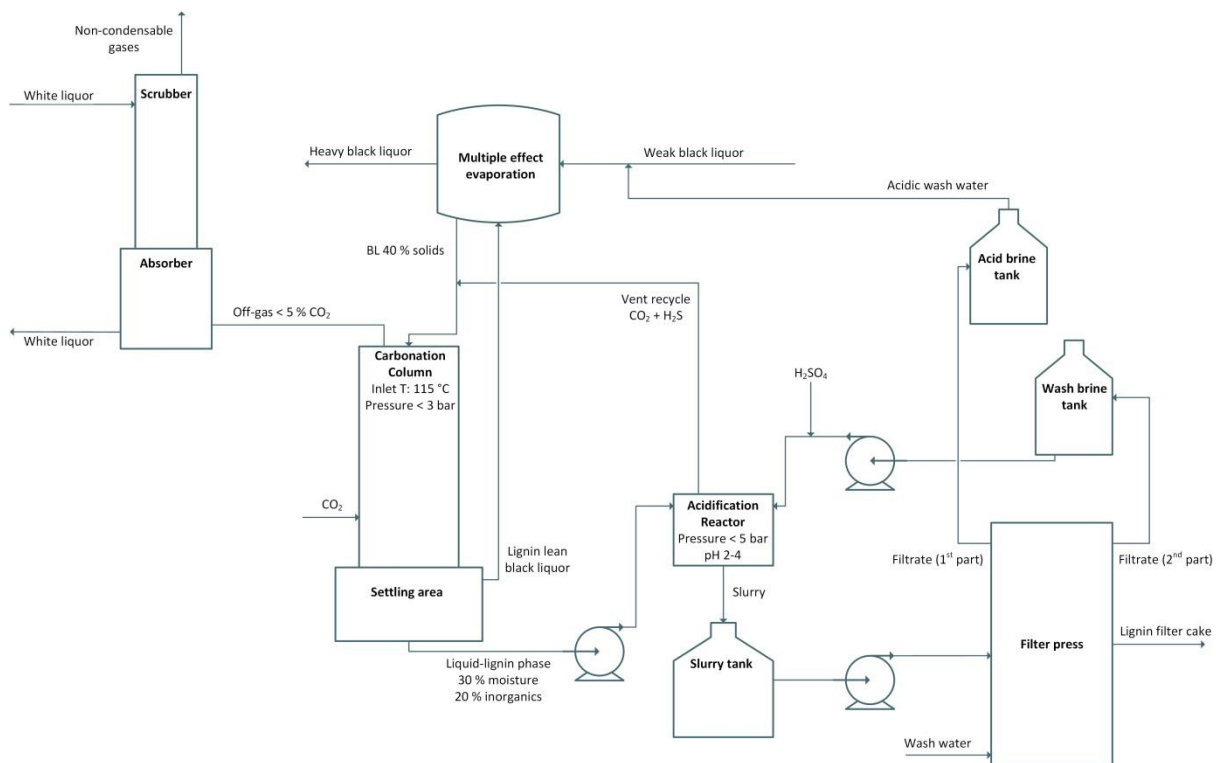A depiction of the LignoBoost process is shown in Figure 8.

Figure 8. Detailed process scheme of the SLRP lignin isolation system.

Lignin precipitation

Feed BL is withdrawn after the soap separator at about 40 % DS and pumped to the combined carbonation/settler column where it is contacted with fresh CO_2 and vent gases from the acidification reactor (CO_2+H_2S) to reach a final pH of 9-10. The reported demand of fresh CO_2 for acidification is 170 kg CO_2 per tonne lignin [49]. The temperature in the carbonation column is 115 °C, and the pressure is increased to prevent boiling (no more than 4 bar). In the carbonation column CO_2 is led counter currently to the BL stream and liquid lignin droplets are formed which coalesce as they settle due to gravity. The absorption of acidic gases is very efficient and no more than 5 % of the introduced CO_2 is lost to the venting system [50]. The two-liquid mixture thus undergoes a phase separation into a dense liquid-lignin phase at the bottom of the settler and a lighter lignin-lean liquor which is returned to the liquor evaporation train. The two phases are separated by decantation. The interface can be easily detected with an in-line viscometer. The higher temperature of the returned liquor due to the exothermic neutralization reaction is a main advantage of the SLRP process compared to similar methods [51]. The water content of the liquid lignin fraction is in the range of 30 % and the ash amounts to around 20 % [50].

The vent gases exiting the carbonation column at the top contain CO_2, H_2S and other reduced sulphur compounds. They are led to an absorber unit with a scrubber containing random packings directly on top where they are contacted counter-currently with white liquor. The cleaned off-gas is led directly to the recovery boiler. [50]

Second acidification, filtration and washing

In a next step, the liquid-lignin phase is acidified with approx. 170 kg sulphuric acid per tonne lignin to a pH of 2-3 in a small agitated acidification reactor [49]. The pressure in the acidification reactor is < 6 bar and high enough to prevent boiling at the high temperature. Due to the rapid acidification, CO_2 and H_2S gas are formed instantaneously. They are then led back to the black liquor feed, directly before the entrance to the carbonation column, where the addition of these gases reduces the necessary amount of fresh CO_2 by up to 30 % compared to similar processes [50]. In the acidification reactor the liquid lignin phase solidifies and forms large brown lignin particles. This product suspension is then pumped to a lignin slurry tank (acting as a buffer for the batch-wise operated filter press) and finally filtered and water washed in a plate and frame filter press. Subsequently the filter cake is squeezed with pressure membranes to additionally reduce the moisture content. The first, acidic filtrate is then recycled to the evaporation train, while the wash filtrate is cycled back to the acidification reactor after addition of concentrated H_2SO_4.

During the carbonation stage, it is possible to generate different lignin fractions by step-wise reduction of the BL pH with predetermined amounts of CO_2 for acidification. Thus fractions with a narrower range of molecular weight can be tailor-made for different applications [52]

For the production of dry lignin with an ash content of 1.1 %, a fresh wash water requirement of 1.36 m³ per tonne of lignin is reported [49]. In general the ash content can be decreased to desired values for specific applications by varying the amount of wash water used. This is of course true for all the lignin extraction processes discussed in this section.

2.1.2.4   *Influencing factors and points to consider*

Depending on the degree of acidification, temperature, mixing speed, CO_2 concentration and flowrate as well as black liquor composition, the acidification time to reach the desired final pH can differ widely. Wallmo and coworkers of the LignoBoost team found an acidification time of around 12 min to reach pH 10 at a stirring speed of 200 rpm upon use of pure CO_2 gas for acidification in a simple stirred tank reactor. In experiments where a mixture of 15 % CO_2 and 85 % N_2 was used, they report an acidification time of 100 min in order to reach pH 10 at a mixing speed of 150 rpm. Faster mixing was not possible due to foaming issues. Both experiments were carried out using softwood BL with a starting pH of 13.6 and a precipitation temperature of 75 °C and atmospheric pressure. The gas flowrate was 1 L·min^{-1} for 2 kg of BL [30].

Important parameters influencing the lignin precipitation yield are solids content of BL, temperature, ionic strength, precipitation pH and average molecular weight of lignin [53]. Using precipitation with CO_2, the pH dependent yield of lignin precipitated from softwood liquor lies in the range of 30 to 80 % as reported by Zhu and Theliander, at 65 °C and a precipitation pH of 11 to 9.5, respectively. They also showed that the precipitation yield can be significantly increased by an increase of ionic strength [53]. Use of this correlation is described in a patent application granted in 2013 to Öhman et.al.. The applicants claim the addition of sulphate salts like Na_2SO_4 and $CaSO_4$ to the BL, in addition to acidification to a pH<9.5, in order to promote lignin precipitation and to increase the yield. For BL with 30 % DS they reported a lignin yield of approx. 60.5 % upon precipitation at 80 °C with CO_2 to a final pH of 9.6 compared to 66.8 % yield after addition of 50 g Na_2SO_4 per litre of BL under otherwise similar conditions [54].

The lignin yield as well as the lignin filterability is reported to increase with higher solids content of the BL. Furthermore, the filtration resistance increases for higher soap content in the feed liquor [45].

The filtration resistance of the slurry after precipitation was investigated in several different studies conducted by the groups involved in the development of the LignoBoost and the LignoForce system [28], [55]–[57]. They found that the filterability of the lignin precipitate is not only depending on it's origin and composition like dry substance content and residual tall oil soap, but also on the

precipitation conditions. Wallmo et.al. discovered that a high content of hemicelluloses in the initial BL impairs the filtration properties. Black liquor with a hemicellulose concentration of approx. 5 $g \cdot L^{-1}$ had a filtration resistance in the order of 10^{10} $m \cdot kg^{-1}$, while a BL with approx. 14 $g \cdot L^{-1}$ hemicellulose had a filtration resistance in the order of 10^{13} $m \cdot kg^{-1}$. Reducing the hemicellulose content by heat treatment or membrane filtration prior to precipitation could significantly reduce the filtration resistance. Furthermore they reported a decrease of filtration resistance with decreasing precipitation pH [56].

Kannangara and coworkers conducted a thorough study on the effect of mixing hydrodynamics during the precipitation and ageing stage. They found a strong influence of the turbulent shear rate on size and shape of precipitate and thus filtration properties [55]. Their experimental set-up was an open vessel equipped with two different stirrers and a sparger for CO_2 introduction at the bottom of the vessel. They found that a high power input, and thus high Re number, during the acidification (around 1 $kW \cdot m^{-3}$) and a low power input (around 0.003 $kW \cdot m^{-3}$) throughout the ageing step led to formation of the largest and densest particles with the best filterability during the first filtration as well as the washing step. The primary lignin nuclei formed comprised a size range of 1-2 µm and the primary lignin agglomerates measured directly after the finished acidification varied in size from 10-20 µm median diameter. For the primary agglomerates, acidification at higher power input led to smaller but denser aggregates. During the ageing step, the particle size increased depending on the power input to about 50-60 µm median diameter. No further increase of particle agglomerate size was detected after an ageing time of 20-30 minutes. The lowest filtration resistance reported was $1.83 \cdot 10^9$ $m \cdot kg^{-1}$ for the arrangement with high shear during acidification and low shear during ageing, with a highest filtration rate of 243 $kg \cdot h^{-1} \cdot m^{-2}$ [55].

2.1.2.5   *Distinguishing features of the three state of the art processes*

The following section gives a short summary of the basic acidification process and the three state of the art processes described above. In Table 1 the advantages and disadvantages of the three processes are listed, together with the stated amounts of washing water and the resulting ash content of the lignin product.

Basic process [25], [26]

- Acidification of a portion of the black liquor stream (DS content of 20-45 %) using H_2SO_4 or CO_2 to a final pH of 10 to 8
- Separation of precipitated lignin from lignin lean liquor by filtration, recirculation of the lignin lean liquor to the liquor cycle
- Initial washing with acidic washing water (typically acidified with H_2SO_4) to reduce sodium content, followed by water wash

- Limitations: Emission of H_2S and other odorous TRS compounds; high filtration resistance during acid wash; high ash content due to residual sodium and inefficient washing

LignoBoost [25]

- Basic process including acidification with preferably CO_2, followed by a first filtration step and recirculation of lignin lean liquor to the liquor cycle
- Re-slurrying of lignin filter cake and acidification of slurry to final washing pH (pH 1-4) with H_2SO_4
- Second filtration step and washing of filter cake with dilute H_2SO_4 solution

LignoForce [42]

- Black liquor is partially oxidized with a suitable agent prior to the basic precipitation process as described above

SLRP [50]

- Lignin is precipitated from black liquor using CO_2 under increased pressure and temperature, leading to a true liquid lignin phase separated from the lignin lean residual black liquor phase
- The liquid lignin phase is decanted from the aqueous phase and further acidified using H_2SO_4 leading to formation of a solid precipitate
- The solid lignin precipitate is separated from the residual aqueous phase by filtration
- The lignin filter cake is washed with dilute acid and water like in the basic process

Table 1. Wash water requirements as well as advantages and disadvantages of the three state of the art processes discussed above.

	Wash water demand [m³/t lignin] \ lignin ash content [%]	Advantages	Disadvantages
LignoBoost	2-2.5 m³ \ 0.2-1.4 %	+ Improved filtration properties + Low ash content + Increased lignin yield	− Second filter press necessary − Release of odorous compounds
LignoForce	10-15 m³ \ 0.07-0.18 %	+ Improved filtration properties + Low ash content + Lower acid consumption + Less odor emission	− Lower lignin yield − Oxygen requirements − SO_2 emissions
SLRP	1.36 m³ \ 1.1 %	+ Improved filtration properties + Low ash content + Continuous process + Effective vent recycle + High temperature of recycled LLBL	− Lower energy efficiency − Operation under increased pressure

2.2   Other isolation processes

Following acid precipitation, lignin extraction by membrane processes is the method most discussed in the literature. For lignin separation typically ultrafiltration or nanofiltration membranes with varying cut-off can be used [21], [23]. There are also studies on acid precipitation of lignin previously concentrated by ultrafiltration. However, a major drawback of membrane processes is the tendency of lignin to adhere to the membrane surfaces, which increases the resistance and makes regular cleaning of the membranes necessary [23].

Electrolysis of lignin can lead to in situ coagulation of lignin, similar as in acid precipitation. However, the process is energy intensive and problems due to membrane fouling have been reported, while the issue of separation of coagulated lignin remains unsolved [23].

Solvent extraction for lignin isolation has been investigated on lab-scale. The use of water immiscible solvents like dichloromethane led to a partial coagulation of Kraft lignin with acceptable filtration properties. Water soluble solvents like ethanol and methanol were also investigated, their application led to precipitation of up to 60 % of dissolved lignin. However, so far no efficient methods for solvent recovery have been proposed, hence these methods are still not applicable for lignin isolation on larger scale. [23]

3 Basics

3.1 Titration

3.1.1 Acid-base reactions

In a generalized definition an acid-base reaction is an equilibrium reaction. An acid generates H^+ (or, to be more accurate, H_3O^+) ions either by releasing the ions itself (e.g. HCl) or by taking up OH^- ions from water molecules (e.g. metal ions like Al^{3+}). A base can form OH^- ions in the same way. The change in pH of an aqueous solution is restricted by the equilibrium condition for water:

$$K_w = [H_3O^+] \cdot [OH^-] = 10^{-14} \frac{mol^2}{L^2} \; (at \; 25 \, °C)$$

Equation 3

With

- K_w: equilibrium constant of water [mol²·L⁻²]
- $[H_3O^+]$: concentration of H_3O^+ ions [mol·L⁻¹]
- $[OH^-]$: concentration of OH^- ions [mol·L⁻¹]

The pH of an aqueous solution is defined as $-\log[H_3O^+]$, while the pOH equals $-\log[OH^-]$. In accordance with Equation 3, the sum of both values always gives 14. The dissociation behaviour of acids and bases is controlled by their respective dissociation equilibrium, too. For a strong acid (or base), the equilibrium constant for the reaction

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

Equation 4

is very high and only the products on the right-hand side are present in aqueous solution. Hence, the concentration of H_3O^+ ions equals the concentration of dissolved base and the calculation of the respective pH is easy. If an acid is not monobasic like HCl but polybasic like H_2SO_4, it needs to be considered that it generates two or more H_3O^+ ions upon dissolution.

Substances that do not dissociate completely are called weak acids or bases, the dissociation of a weak acid is controlled by the chemical equilibrium. The equilibrium constant for such a weak acid is given by Equation 5.

$$K_a = \frac{[H_3O^+] \cdot [A^-]}{[HA]}$$

Equation 5

With

- K_a: equilibrium constant of acid HA [mol·L⁻¹]
- $[A^-]$: concentration of conjugate base of acid HA [mol·L⁻¹]
- $[HA]$: concentration of undissociated acid HA [mol·L⁻¹]

The degree of dissociation or "strength" of an acid upon dissolution can be described by its equilibrium constant of dissociation according to Equation 6.

$$pK_a = -\log(K_a)$$

An acid with a very low pK_a value will form a comparably acidic solution upon dissolution, while an acid with a high pK_a will hardly dissociate at all in neutral water. However, a lower acidity for a certain acid means that the conjugate base is stronger. The basicity of a substance is described by its pK_b, in accordance to the pK_a of the acid. Like for the dissociation of water, the sum of pK_a and pK_b of an acid and conjugate base pair is always 14. For example, phenol is a very weak acid with a pK_a of around 10 [58], but the conjugated base phenolate is considerably stronger, since it has a pK_b of approx. 4.

If a base BOH is added to a solution of an acid, the acid will react with the base to form the corresponding salt and water according to Equation 7.

$$HA + BOH \rightarrow H_2O + A^- + B^+$$

If a considerably stronger acid is added in excess to a solution of a weaker acid, the weak acid will be "pushed" completely into the un-dissociated form and the pH of the solution will be determined only by the concentration of the stronger acid.

3.1.2   Titration analysis

Titration experiments can be performed to determine the concentrations of dissolved acids or bases. The standard used to titrate the sample solution is a strong acid or base, like HCl and NaOH with a defined concentration. Depending on their pK_a or pK_b values, the acids or bases present in the sample will be neutralized one after the other. The acid with the lowest - or base with the highest - pK_a will be neutralized first, hence strong acids and bases that are completely dissociated are neutralized first. When a strong acid is titrated with a strong base, the pH of the solution will be determined by the remaining concentration of acid, or, in case all the acid in the sample has been neutralized, by the concentration of surplus titration standard. Throughout the neutralization of a weak acid by a strong base, the concentration of un-dissociated acid and conjugate base do not solely depend on the pK_a anymore but on the amount of titration standard added. After the molar equivalent of strong base has been added to the weak acid, it will be completely in the form of the conjugate base. However, before this point, the two species of the acid will be present in parallel. The pH of such a solution containing both acid and conjugate base can be estimated from the so-called Henderson-Hasselbalch equation (Equation 8). This equation describes the pH value of a buffer solution.

$$pH = pK_a + \log\left(\frac{A^-}{HA}\right)$$

An acid/conjugate base pair is called buffer, because in the pH range of the pKₐ the pH does only change slowly when a strong acid or base is added. However, as soon as the weak acid or conjugate base has been completely neutralized by a strong acid or base, the buffering effect vanishes. Therefore, the higher the overall concentration of buffering pair, the higher is the buffer capacity. The pH of the buffer is independent of the overall concentration, it only depends on the ratio of the two species and the pKₐ. From Equation 8 it can be deduced that the pH of the solution equals the pKₐ when exactly 50 % of the acid are neutralized. In case of a sample containing multiple acidic or basic compounds, the concentrations and pKₐ values of these compounds can be determined by titration, as long as the pKₐ values lie far enough apart. If the pKₐs are too close (closer than ~3 units), the buffering regions will overlap, rendering the interpretation for the individual compounds impossible. In BL samples the pKₐ values of the relevant compounds, i.e. NaOH, lignin Ph-OH groups and H_2S, are far enough apart to guarantee convenient evaluation by titration experiments.

BL samples have a very high initial pH in the range of 13, titration can be carried out with 1 M HCl standard solution. From the generated titration data, the following information can be deduced:

Acid consumption: From the consumed amount of HCl required to reach a certain pH during titration, the amount of acidifier to reach the final pH during the actual precipitation can be readily calculated according to Equation 9.

$$\frac{n_{H^+}}{m_{BL}} = \frac{c_{HCl} \cdot V_{HCl}}{m_{BL}}$$

<div align="right">**Equation 9**</div>

With
- n_{H^+}: moles of hydrogen ions required to acidify BL to final pH [mol]
- m_{BL}: mass of black liquor sample titrated [kg]
- c_{HCl}: concentration of HCl in the standard solution [mo·L⁻¹]
- V_{HCl}: volume of HCl consumed for titration of m_{BL} to reach final pH [L]

pKₐ and concentration: Titration generates a set of data for pH and corresponding amount of acid or base added. The inflection points of the resulting plot can be employed to determine the equivalence point, where an acidic group in the solution is completely protonated or deprotonated. The inflection points of a titration curve are determined by formation of the first derivative, given by Equation 10. The maxima of the resulting graph of dpH/dV_{HCl} vs V_{HCl} correspond to the inflection points. Another option is to form the second derivative given by Equation 11, which is then plotted against V_{HCl}. The intersection of this curve with the x-axis gives the maxima of the first derivative and thus again the inflection points.

$$\frac{dpH}{dV_{HCl}} \approx \frac{\Delta pH}{\Delta V_{HCl}}$$

<div align="right">**Equation 10**</div>

$$\frac{d^2 pH}{dV_{HCl}^2} \approx \frac{\Delta \left(\frac{\Delta pH}{\Delta V_{HCl}}\right)}{\Delta V_{HCl}}$$

<div align="right">**Equation 11**</div>

With

- ΔpH: absolute difference between two consecutive pH values of the titration plot [-]
- ΔV_{HCl}: absolute difference between two consecutive titration standard volumes of the titration plot [m³]

Following the identification of the inflection points, the concentrations of the different weak bases dissolved in black liquor can be determined. The procedure is the same as for the calculation of total acid consumption from Equation 9. The moles of HCl that need to be added to the sample to reduce the pH from one inflection point to the next correspond to the amount necessary to completely neutralize the compound whose pK$_a$ value is between those two points. The concentration of base, c_B, is then calculated from Equation 12, where ip1 and ip2 stand for inflection point 1 and inflection point 2.

$$c_B = \frac{\left(V_{HCl,ip2} - V_{HCl,ip1}\right) \cdot c_{HCl}}{m_{BL}}$$

<div align="right">**Equation 12**</div>

With knowledge of the equivalence points, the pK$_a$ values of the different acidic or basic components dissolved in the sample can be calculated. The pK$_a$ of a base lies between the equivalence point of the more basic substance (in case a base is titrated with a strong acid) and the equivalence point of the base in question. At that point, the pH equals the pKa because 50 % of the weak base are protonated

In case of neutralization of lignin phenolic OH-groups, c$_B$ equals the concentration of Ph-OH in the BL. Based on the UV-lignin content of BL, the moles of Ph-OH per kg of lignin can be calculated according to Equation 13.

$$c_{Ph-OH,lignin} = \frac{c_B}{\frac{c_{lignin,BL}}{\rho_{BL}}}$$

<div align="right">**Equation 13**</div>

With

- $c_{Ph-OH,lignin}$: molar concentration of Ph-OH per lignin mass [mol·kg⁻¹]
- $c_{lignin,BL}$: UV-lignin concentration in BL [kg·L⁻¹]
- ρ_{BL}: density of BL at 25 °C [kg·L⁻¹]

3.2 Filtration

Filtration and washing of precipitated lignin is one of the most critical steps of lignin isolation. If the feed properties and process conditions are not in a proper range, the lignin product is very fine or soft and sticky, making it hard to filter [26], [55]. Assessment of the filtration properties of different lignin products is thus a crucial part of process evaluation.

Since the purpose behind the filtration step during lignin isolation is the recovery of a solid product, cross-flow or deep-bed filtration are not applicable, cake filtration (or dead-end filtration) is the only reasonable option. In cake filtration, the suspended solid is deposited on the filter media and the cake height increases with increasing filtrate volume. Initially, the particle size retained is determined by the pore size of the filter media used, but after an initial built-up period, the cake itself functions as filter media and also smaller particles can be retained.

The pressure drop across the filter cake depends on the filtrate flow rate, the filter area, the filter cake height, the liquid viscosity and the specific filter cake resistance. The resistance of flow through a porous media can be described by Darcy's law [59]:

$$\Delta p_c = \frac{\dot{V}}{A} \cdot H \cdot \eta \cdot \alpha_H$$

Equation 14

With

- $\dot{V}$: filtrate flow rate [m³·s⁻¹]
- Δp_c: pressure drop over the filter cake [Pa]
- A: filter area [m²]
- H: filter cake height [m]
- η: filtrate viscosity [Pa·s]
- α_H: specific filter cake resistance [m⁻²]

Not only the filter cake, but also the filter medium can be considered a porous medium and adds to the overall pressure drop. The influence of the medium, which has a constant height is described by Equation 15:

$$\Delta p_m = \frac{\dot{V}}{A} \cdot \eta \cdot \beta$$

Equation 15

With

- β: resistance of the filter medium [m⁻¹]
- Δp_m: pressure drop over the filter medium [Pa]

In many cases the resistance of the filter medium is several orders of magnitude lower than that of the filter cake and is thus negligible compared to the latter. This is usually also valid for filtration of precipitated lignin.

Summing up the pressure drop caused by the filter cake and the filter medium gives the total pressure drop Δp:

$$\Delta p = \Delta p_c + \Delta p_m = \frac{\dot{V}}{A} \cdot H \cdot \eta \cdot \alpha_H + \frac{\dot{V}}{A} \cdot \eta \cdot \beta \qquad \text{Equation 16}$$

While the resistance of the filter medium is constant, the pressure drop caused by the filter cake increases with cake built-up, since also the cake height increases. In case of a homogeneously mixed suspension, the cake height is given by Equation 17:

$$H = \frac{V_c}{A} = \frac{K_H \cdot V}{A} \qquad \text{Equation 17}$$

With

- V: filtrate volume [m³]
- V_c: filter cake volume [m³]
- $K_H = \frac{V_c}{V}$: factor describing the cake volume per filtrate volume; it depends on the solidosity of the feed suspension and the cake porosity [-]

A combination of Equation 16 and Equation 17 gives the cake filter equation:

$$\Delta p = \frac{\eta \cdot K_H \cdot \alpha_H \cdot V}{A^2} \cdot \frac{dV}{dt} + \frac{\beta \cdot \eta}{A} \cdot \frac{dV}{dt} \qquad \text{Equation 18}$$

With

- t: filtration time [s]

For determination of the filter cake and filter media resistance, the integrated versions of the above equation are usually used, either for constant filtrate flow rate (Equation 19) or for constant pressure drop (Equation 20), which is more common because the experimental set-up is much easier.

$$\Delta p = \eta \cdot \frac{\dot{V}}{A} \cdot \left(\frac{K_H \cdot \alpha_H}{A} \cdot V + \beta \right) \qquad \text{Equation 19}$$

$$t = \frac{\eta \cdot K_H \cdot \alpha_H}{A^2 \cdot \Delta p} \cdot V^2 + \frac{\beta \cdot \eta}{A \cdot \Delta p} \cdot V \qquad \text{Equation 20}$$

A plot of t/V versus V gives a linear equation (Equation 21) with the slope a and intercept b of the integrated Darcy equation for constant pressure drop.

$$\frac{t}{V} = a \cdot V + b \qquad\qquad \textbf{Equation 21}$$

Rearrangement of the equations for *a* and *b* gives correlations for calculation of filter cake resistance α_H (Equation 22) and filter media resistance β (Equation 23), respectively.

$$\alpha_H = a \cdot \frac{2 \cdot A^2 \cdot \Delta p}{\eta \cdot K_H} \qquad\qquad \textbf{Equation 22}$$

$$\beta = b \cdot \frac{A \cdot \Delta p}{\eta} \qquad\qquad \textbf{Equation 23}$$

The viscosity η of the filtrate has to be measured for the filtration temperature of the slurry. For determination of K_H, which is a measure for slurry solids content and cake porosity, the filter cake height H_t for a certain filtrate volume V_t has to be determined experimentally before Equation 24 can be solved.

$$K_H = \frac{H_t \cdot A}{V_t} \qquad\qquad \textbf{Equation 24}$$

In the literature, the filter cake resistance is often based on the solids load of the initial slurry, K_M [kg·m^{-3}], instead of K_H. This than gives the filter cake resistance α_M [m·kg^{-1}], which can be calculated from α_H according to Equation 25 and Equation 26.

$$K_M = \frac{m_{lignin,c}}{V} \qquad\qquad \textbf{Equation 25}$$

$$\alpha_M = \frac{\alpha_H \cdot K_H}{K_M} \qquad\qquad \textbf{Equation 26}$$

With

- $m_{lignin,c}$: lignin mass in the filter cake [s]
- K_M: Solids load of feed slurry [kg·m^{-3}]
- α_M: specific filter cake resistance [m·kg^{-1}]

Generally, the resistance of a porous media to liquid flow depends on the particle size, size distribution and structure, which all influence the porosity of the resulting cake. For lignin filter cakes, the resistance is also influenced by the pH and the ionic strength of the solution, since the particle-particle interactions strongly depend on these parameters. Durruty et.al. showed that the solidosity (solid volume fraction) of the filtered slurry has no influence on the filterability of the resulting product. However, the filterability of lignin weakly depends on the applied pressure. An increase in filtration pressure led to slight compression of the cake and hence lower porosity and higher filter resistance [60]. For compressible filter cakes, there is often a thin, compressed layer facing the filter medium.

This layer forms throughout the filtration and is thereafter responsible for the resistance to flow due to its low porosity [59].

Helander et.al. showed that lignin precipitated from weak BL was very difficult to filter. An increase of the ionic strength was necessary to yield a filterable product. Therefore, the use of concentrated black liquor, typically to 30-40 % solids content, not only increases the lignin yield but also the filterability thereof [61].

4   Materials and methods

4.1   Materials

In this section the various chemicals and raw materials used throughout the experimental work are listed.

Black liquor obtained from a local pulp and paper mill:

Intermediate solids content – extracted after first evaporation unit

NaOH (J.T.Baker, now part of Thermo Fisher Scientific):

solid pellets
purity: min 98 %

1 M HCl (Merck):

Titrisol® solution
purity: 1.000 mol·L^{-1} (20 °C)

CO$_2$ (Linde):

technical gas

N$_2$ (Air-Liquide):

Alphagaz^{TM}
purity ≥99.999 %

4.2   Characterization of black liquor, filtrates and lignin

The density and dynamic viscosity of the liquid samples were determined at temperatures between 20 and 70 °C using an Anton Paar SVM 3000 Stabinger Viscometer (Graz, Austria). The pH was measured with a WTW Sentix 42 pH electrode (Wilheim, Germany).

4.3   Spectrophotometric determination of lignin content

The lignin content of the liquid samples was estimated using UV/VIS spectrophotometry. The samples were diluted with 0.1 N NaOH in order to assure a consistent pH of the measured solutions. Depending on the lignin content of the samples, the dilution factor was between 1000 and 3000, yielding an absorbance of 0.3-1.5. The measurement was performed at room temperature (RT) in PP UV-cuvettes with 10 mm transmitted path length, using a Shimadzu UV-1800 Spectrophotometer (Kyoto, Japan). Absorbance was measured at 280 nm, the wavelength of maximum absorbance. An absorption coefficient of 23.7 L·g^{-1}·cm^{-1} was used to calculate the UV-lignin content [55]. The measurements were performed in triplicate.

4.4   Total solids content

The content of dissolved and suspended solids was determined as reported in the literature [56]. A ceramic crucible was dried for 2 h at 105 °C in a drying oven before it was cooled to RT in a desiccator. The tare was noted and a weighed sample aliquot of 1-5 g was transferred to the crucible. The crucible was again placed in the oven at 105 °C and dried to constant weight. The final mass (again weighed after cooling in the desiccator) was used to calculate the total solids content of the samples according to Equation 27:

$$DS\ [\%] = \frac{m_{out} - m_{tara}}{m_0} \cdot 100$$

Equation 27

With

- m_{out}: mass of dry sample and crucible after drying [g]
- m_{tara}: dry mass of crucible [g]
- m_0: wet sample mass [g]

4.5   Titration

The titration of black liquor was carried out manually; the experimental set-up is depicted in Figure 9. About 50 g of sample were weighed into a 200-mL glass beaker that was then fixed inside a water bath above a magnetic stirrer with temperature control. Both the water bath and the sample were equipped with a stirring bar to assure sufficient mixing. A WTW Sentix 42 pH electrode was placed inside the sample liquid for pH and temperature measurement. A 1 M HCl solution was applied as titration standard; it was filled into a 50-mL glass burette whose outlet tap was positioned above the sample beaker. Throughout the titration, the sample temperature was controlled by adjusting the water bath temperature. The titration was carried out at 25, 50 and 70 °C with a temperature variation of no more than ±1 °C throughout the experiment. Standard solution was added to the sample in aliquots of around 1 mL, the exact volume was noted after each addition. The sample was then stirred for ½ minutes until the pH was constant, thereafter pH and sample temperature were noted before the next aliquot of standard solution was added.
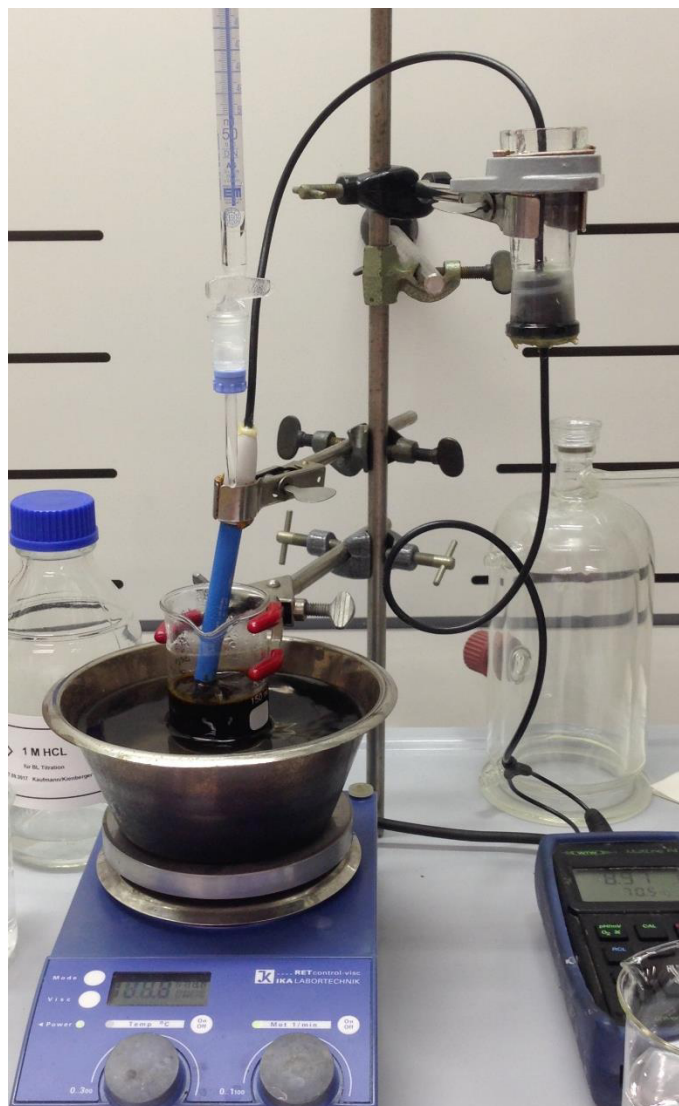
Figure 9. Set-up of the black liquor titration experiments.

4.6   Experimental set-up lignin precipitation

4.6.1   Lab-scale set-up

Preliminary experiments for lignin precipitation were carried out on lab scale, the corresponding reactor is shown in Figure 10. A glass vessel designed for a liquid volume of 1 L with a glass heating jacked (1) connected to a mgw LAUDA thermostat (Lauda-Königshofen, Germany) was equipped with a glass lid (2) and agitated with a propeller (3) operated with an external motor. pH and temperature were monitored with a WTW Sentix 42 pH electrode (4) throughout the precipitation experiment. Pure CO_2 gas was introduced through a Teflon pipe (5) with the outlet at the bottom of the vessel close to the propeller in order to assure proper gas dispersion. The discharge outlet was positioned at the bottom of the reactor vessel (6).

Precipitation conditions:

－   Gas flow rate, monitored with a flowmeter: 50 L·h^{-1}

- Precipitation temperature: 70 °C

- Final pH (measured at 70 °C): 9.5-8.7

- Initial black liquor volume: approx. 1 L

Unless stated otherwise, the slurry was aged for ½ hours at 60 °C after the final precipitation pH was reached. During the ageing period, the mixing speed was reduced in order to promote aggregation of lignin particles.

Figure 10. Set up of the lab-scale precipitation reactor. The reactor (here shown charged with BL) consists of a glass vessel with heating jacket (1), glas lid (2), propeller (3), pH electrode and temperature sensor (4), CO_2 inlet pipe (5), bottom outlet (6).

Following the precipitation procedure, the slurry was discharged through the outlet at the bottom. Throughout the discharge the slurry remaining in the reactor was stirred, since otherwise the outlet orifice was immediately clogged by lignin sediment. Thereafter, the slurry was cooled to 40-30 °C and filtered using a Buchner funnel and filtration flask connected to a Welch Ilmvac LVS 310-p vacuum system (Fürstenfeldbruck, Germany). The filtration speed for the precipitate was only assessed

qualitatively, so no filter cake resistance was determined. The filter cake could then be washed using distilled water at RT, the initial filtrate (LLBL) and the wash filtrate were collected separately.

The slurry, LLBL and lignin filter cake were weighed in order to compute an approximate mass balance. LLBL and filter cake were in some cases used for determination of dry substance content.

4.6.2   Pilot-scale set up

The experimental set-up of the pilot-scale precipitation equipment is described in more detail in the diploma thesis of Andreas Pirschner [62]. The cylindrical glass precipitation reactor shown in Figure 11 was designed as a mammoth pump with a central rising tube whose top is protruding above the liquid level. The gas inlet was positioned at the lower end of the riser. The ascending gas functioned as driving force for mixing and liquid circulation.

Figure 11. Pilot-scale precipitation reactor filled with BL. Introduction of dilute CO_2 gas led to the formation of foam above the liquid surface.

The reactor was charged with approx. 4.3 kg of black liquor using a peristaltic pump. The black liquor feed had usually been stored in the freezer at -18 °C beforehand and was thawed at room temperature for at least 18 hours. The acidification was achieved either using pure CO_2 gas or a mixture of 16 vol% CO_2 in N_2 gas. The temperature was adjusted with a heating jacket connected to a thermostat. Temperature and pH were monitored with a WTW Sentix 42 pH electrode placed in the black liquor outside of the rising tube. Precipitation was performed discontinuously and took between 20 and 80 min, depending on gas flow rate and CO_2 concentration. The volumetric gas flow rate was between 220 and 300 L·h^{-1} and the final pH (at 70 °C) was typically between 9 and 9.1. For experiments performed with dilute CO_2, the concentration thereof in the reactor off-gas was measured using a Flow^{EVO} NDIR-sensor from smartGAS (Heilbronn, Germany). The residual off-gas contained besides CO_2 (and N_2 in case of dilute feed gas) also evaporated water and H_2S, which is toxic in sufficient concentrations. Hence, the off-gas was channelled in a gas-tight tube-system through a gas wash bottle containing 1 M NaOH solution and thereafter into the off-gas ventilation duct.

Following the precipitation, the resulting slurry was discharged into a canister through a tap at the bottom of the reactor. The slurry was cooled to 30-40 °C and then filtered in the same way as the product suspension of the lab-scale precipitation, described in part 4.6.1. For two experiments (experiments 5 and 6) only representative fractions of the slurry were filtered for balancing, the remaining product was discarded. For determination of the filter cake resistance as described below, approx. 250 mL of well mixed slurry were withdrawn prior to the main filtration. The pH of the LLBL-fractions after filtration of all precipitation experiments was measured again at room temperature.

4.7 Determination of specific filter cake resistance

Representative aliquots of lignin slurry were filtered at constant vacuum pressure. A vacuum resistant glass flask, lid and a Buchner funnel were used for filtration. The set-up is depicted in Figure 12. As filter medium, Macherey-Nagel MN 615 ¼ folded filter papers (Düren; Germany) were applied. This filter paper has an average retention capacity of 4-12 μm particles and medium fast filtration characteristics [63][64]. The Buchner funnel had a filter area diameter of 61.5 mm. The filtrate was collected in a 50-mL graduated cylinder. The filtrate volume and the filtration time were recorded for each experiment, whilst the liquid level in the Buchner funnel was kept constant by addition of sample slurry. This assured a constant hydrostatic pressure. The pressure difference to promote the filtration was applied with a Welch Ilmvac LVS 310-p vacuum system connected to the filtration flask. A pressure difference of only 70-80 mbar was applied, since a higher pressure difference would have led to a too high filtration speed which in turn would have hampered the recording of filtrate volume and time. Following the filtration, the final filtrate volume and filter cake height were recorded.
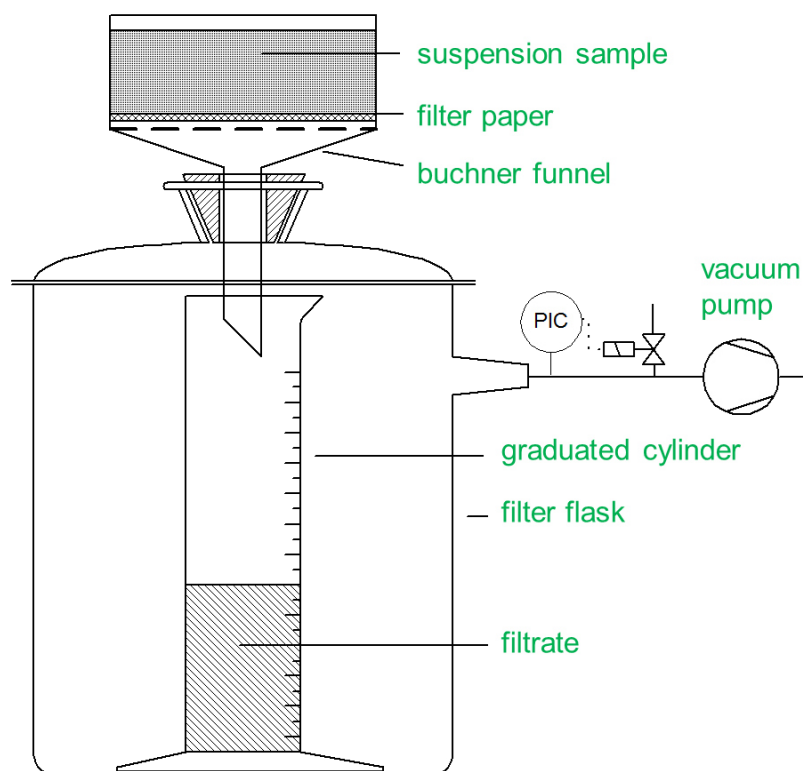
Figure 12. Depiction of experimental set-up for determination of filtration resistance.

4.8   Lignin solubility

For a rough estimation of lignin solubility, unwashed lignin filter cake was used. It was thereafter mixed with a specific amount of deionized water and incubated for a set time on a magnet stirrer at room temperature and 200 rpm. The filter cake aliquots were weighed prior to the experiments and the added amount of water was adjusted depending on the filter cake mass in order to assure a controlled level of dilution. The solids content of the initial cake was approx. 1/3 of the total mass. Thereafter, the suspensions were filtered and the filtrate was analysed for lignin concentration using UV/VIS spectroscopy.

The solubility in dependence of the solvent pH was estimated by suspending an aliquot of filter cake in the same amount of either distilled water or NaOH solution at pH 10 (25 °C). The suspension was stirred for approx. 12 minutes at 40 °C, 200 rpm; the slurry was then filtered and the UV-lignin content of the liquid fraction measured.

5   Results and discussion

5.1   Characterization of black liquor

The determined properties of black liquor obtained from a local pulp and paper mill are summarized in Table 2.

Table 2. Properties of black liquor.

pH (25 °C)	12.92
pH (50 °C)	11.62
pH (70 °C)	10.29
DS [%]	31.5
$c_{Lignin,BL}$ [g L^{-1}]	144.3
density ρ [g·cm^{-3}] (25 °C)	1.1824
density ρ [g·cm^{-3}] (70 °C)	1.1523
viscosity η [mPas] (20 °C)	7.2808
viscosity η [mPas] (70 °C)	2.0869

It has to be taken into account that most of this data has to be considered with care. The pH value usually varied in the range of 0.3 pH units, which might be attributed to variations in temperature (also in gel temperature inside the electrode body) and measurement history. After prolonged measurements, the pH value often showed a large bias, of up to 0.6 pH units, when a calibration buffer was measured for control. The high salt load, organic solids content and temperature of BL altered the measurement accuracy over time.

The determination of DS was difficult since the applicable sample mass was low, leading to higher inaccuracies caused by weighing errors. A sample height exceeding a few millimetres in the crucibles led to inaccurate results and overestimation of solids due to incomplete evaporation of water.

The spectrophotometric measurement of lignin concentration only gives a rough estimation of the actual lignin content. Since the molecular structure of lignin strongly depends on many different factors like biomass source and processing, the use of an absorption coefficient found in the literature is risky. The specific absorption of dissolved lignin molecules at 280 nm depends on the number of aromatic groups, which in turn depends on wood handling and also molecular weight of lignin molecules. For better accuracy, a calibration with a BL and ideally also a LLBL sample of known lignin content would have been required. An additional source of variations is the potential presence of suspended solids in the measured samples. Solids generally impede absorption measurements, but in case of suspended lignin, this dissolves upon sample dilution and thereby introduces further errors due to incomplete dispersion.

5.2   Titration

The titration of BL samples was performed in duplicate at three different temperatures, 25, 50 and 70 °C. The excellent reproducibility is shown in Figure 13, where two separate titration curves are plotted.
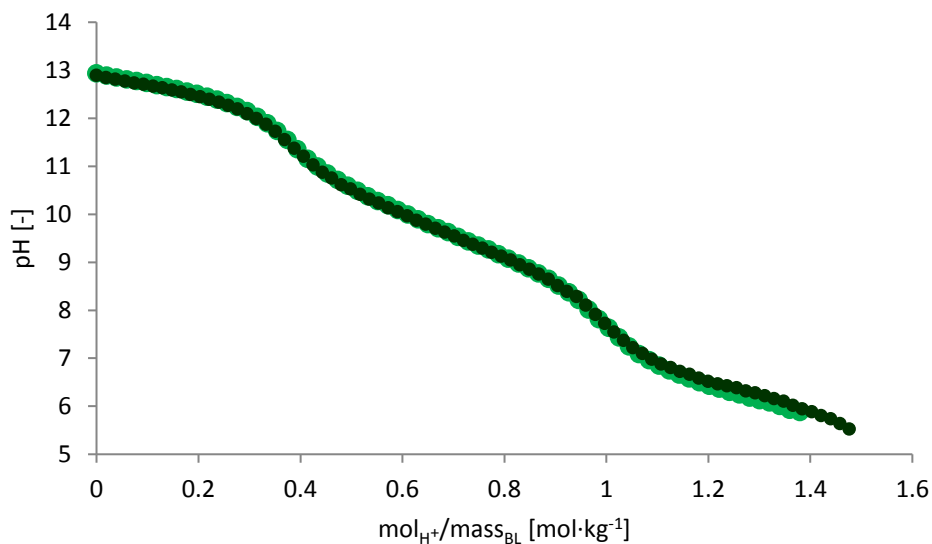
Figure 13. Titration curves of BL with 1 M HCl at 25 °C. The green and turquoise circles represent the duplicate measurement.

The titration curve shows the pH regions where BL has the highest buffer capacity. In the initial pH region, between pH 13 and 12, NaOH neutralisation reactions and the buffering action of Na_2S are responsible for the slow pH decrease. In the region of approx. pH 10.5 to 8.5, the buffering action of phenolic lignin OH-groups becomes dominant. Starting from pH 7 and below, first NaHS and then carboxylic groups of lignin and free carboxylic acids are the main buffering compounds.

For all titration curves measured, the pK_a and concentration of lignin phenolic OH-groups was estimated from the inflection points. For that, the first derivative was calculated from the titration data. The resulting curve is plotted in Figure 14, where all data points were used for calculation of the derivative. Since the small interval led to strong scattering of the data which rendered the identification of the inflection point difficult, a larger interval of three points was chosen for the final evaluation. The corresponding plot is shown in Figure 15, that also shows the relation to the original titration curve.
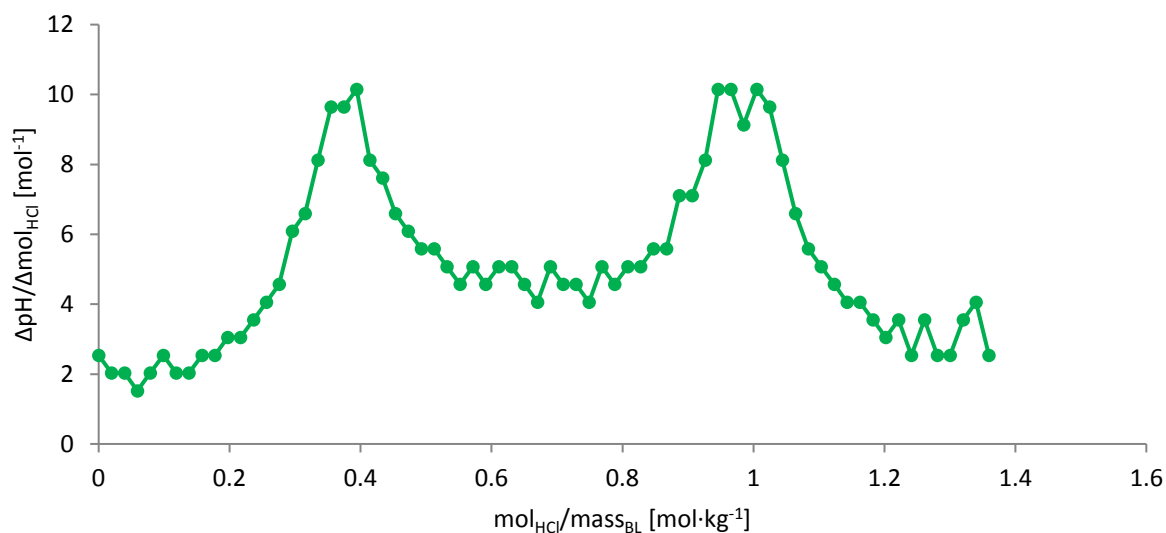
Figure 14. First derivative of the titration data for BL. Titration was performed with 1 M HCl as standard solution at 25 °C.
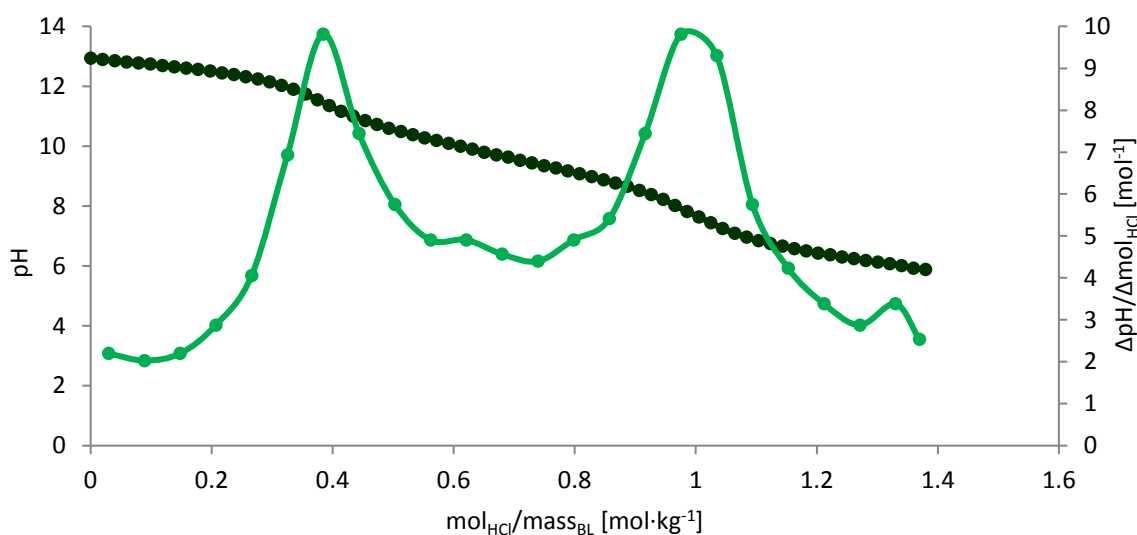
Figure 15. Titration curve (dark green) and first derivative thereof (turquoise). Titration was performed with 1 M HCl as standard solution at 25 °C. The first derivative was calculated using an interval of three data points.

From the first derivative plots the inflection points were estimated and thereof the moles of phenolic OH-groups according to Equation 13. The average pK_a of the phenolic OH was estimated from the pH at the point on the curve between the two inflection points. Figure 16 shows an example for inflection points and pK_a determined from the first derivative of the corresponding curve.

The titration curves for the three different titration temperatures are plotted in Figure 17. The resulting values for pK_a and Ph-OH concentration are summarized in Table 3 and Table 4.
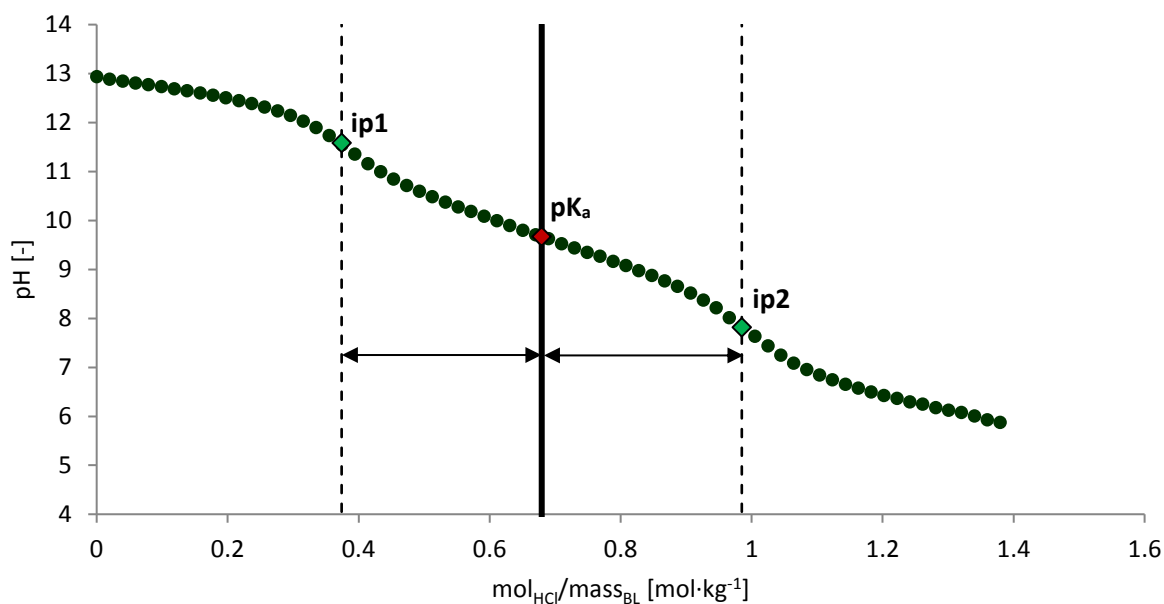
Figure 16. Exemplary titration curve (dark green) showing the determined parameters: turquoise diamonds denote the inflection points; red diamond denotes the pK$_a$, which corresponds to the pH that is exactly in the middle between the two inflection points. Titration was performed with 1 M HCl as standard solution at 25 °C.
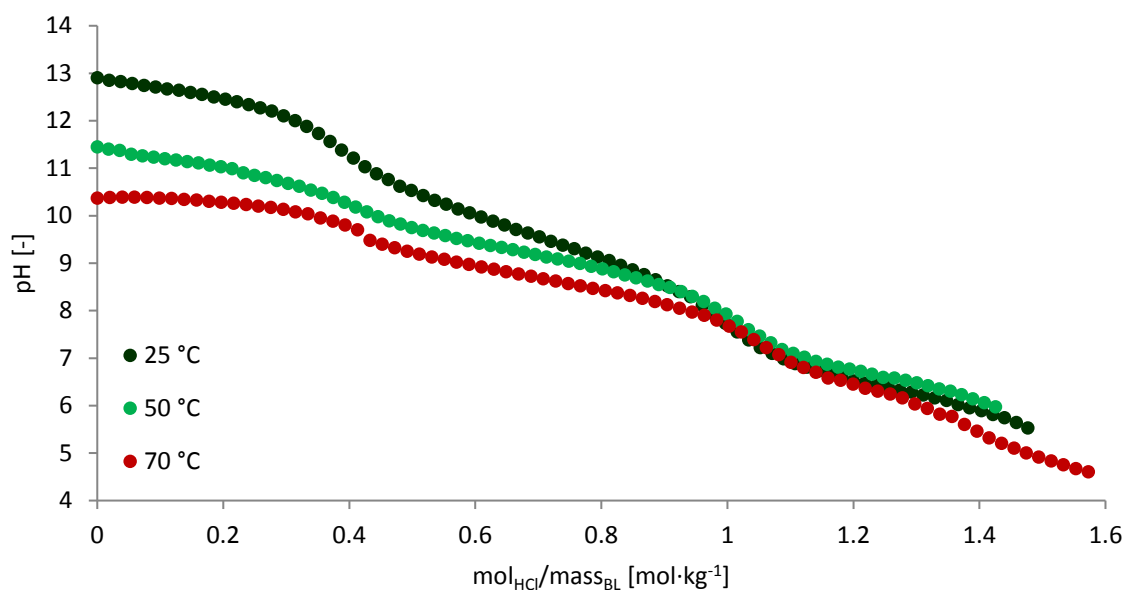
Figure 17. Titration curves of BL at different temperatures. Dark green: titration at 25 °C; turquoise: titration at 50 °C; red: titration at 70 °C. Experiments were carried out with 1 M HCl as standard solution.

Table 3. Summary of estimated Ph-OH content and pK$_a$ of lignin in dependence of temperature. Titration experiments were performed in duplicate ("titration 1" and "titration 2").

	Temperature [°C]	$c_{Ph-OH,lignin}$ [mol kg^{-1}]	pK$_a$ lignin [-]
titration 1	25	5.01	9.67
titration 2		4.89	9.67
titration 1	50	5.16	9.12
titration 2		5.49	9.06
titration 1	70	5.14	8.62
titration 2		5.00	8.65

Table 4. Average Ph-OH content and pK$_a$ of lignin.

Temperature [°C]	c$_{Ph-OH,lignin}$ [mol kg^{-1}]	pK$_a$ lignin [-]
25		9.67
50	5.11 ± 0.21	9.09
70		8.63

The average Ph-OH content in lignin was estimated to be 5.11 mol·kg^{-1}. Wallmo and coworkers, who analysed the phenolic OH content of precipitated and washed LignoBoost lignin spectrophotometrically, reported concentrations between 3.2 and 4.9 mol·kg^{-1} [56]. Kouisni et.al. determined the Ph-OH as well as the total OH-content of lignin isolated with the LignoForce system using ^{31}P NMR measurements. They found Ph-OH concentrations of 1.3-3.3 mol·kg^{-1} of isolated lignin and 4.1-5.7 mol·kg^{-1} of total OH-groups [45]. Although in this thesis the applied method for measurement of the Ph-OH groups was different than those applied by other groups, the resulting value is in the same range. Considering the differences between the analysed lignin fractions, it is to be expected that the Ph-OH content measured by titration of BL is higher than that measured for isolated lignin. A higher concentration of Ph-OH groups is an implication that the average molecular mass of lignin was lower compared to the lignins analysed by the other groups. Since for this work the total amount of dissolved lignin was analysed and the LignoBoost and LignoForce groups only investigated lignin that had already been precipitated, this is a reasonable result. Lignin with a higher molecular mass precipitates at a higher pH than low molecular weight lignin, while the mass based Ph-OH content of lignin increases with decreasing molecular weight [54][65]. Only 40-70 % of the lignin are precipitated in the LignoBoost and LignoForce process, yielding lignin with higher average molar mass and lower relative Ph-OH concentrations.

As shown in Figure 17, the temperature dependency of the titration curves is most distinct in the initial range, where the pH is still high. Towards the end of the titration experiments, the curves converge with decreasing pH. On the one hand, the pH generally changes depending on the temperature. Since the pH equals –log[H$^+$], higher temperature, which is usually associated with a higher degree of dissociation, leads to a higher activity of H$^+$ and thus a lower pH. The extend of the pH change depends on the pH region. At acidic pH the variation is much smaller than in the basic region [66].

On the other hand, BL contains a variety of buffering compounds, most importantly lignin and H$_2$S, but also other carboxylic- or hydroxy-groups of lignin as well as a considerable amount of organic acids like acetic acid [18]. The pK$_a$ values of such weak acids or bases is usually also depending on the temperature and can vary significantly. Those temperature dependencies are mainly responsible for the strong differences between offset and slope of the three titration curves. Kraft Lignin for example has a reported pK$_a$ in the range of 9.4 to 10.8 [18], which strongly depends on the process conditions during Kraft cooking, on the ion strength and thus DS content and on the temperature [53]. Generally,

the pK$_a$ decreases with decreasing molecular weight of lignin. Norgren and Lindström calculated the apparent pK$_a$ values for indulin AT lignin at different temperatures and ionic strength based on UV-absorbance measurements. In 0.1 M NaCl they found a pK$_a$ of 10.4 at 21 °C, 10.1 at 50 °C and 9.8 at 70 °C [65]. While the general trend identified by Norgren and Lindström is similar to the pK$_a$ values found during this work, the span is smaller and the values are considerably higher. This again might be due to the isolation procedure of indulin AT lignin. Another factor that surely influences the pK$_a$ is the ionic strength, which is with 0.1 M NaCl much smaller than in an actual BL sample.
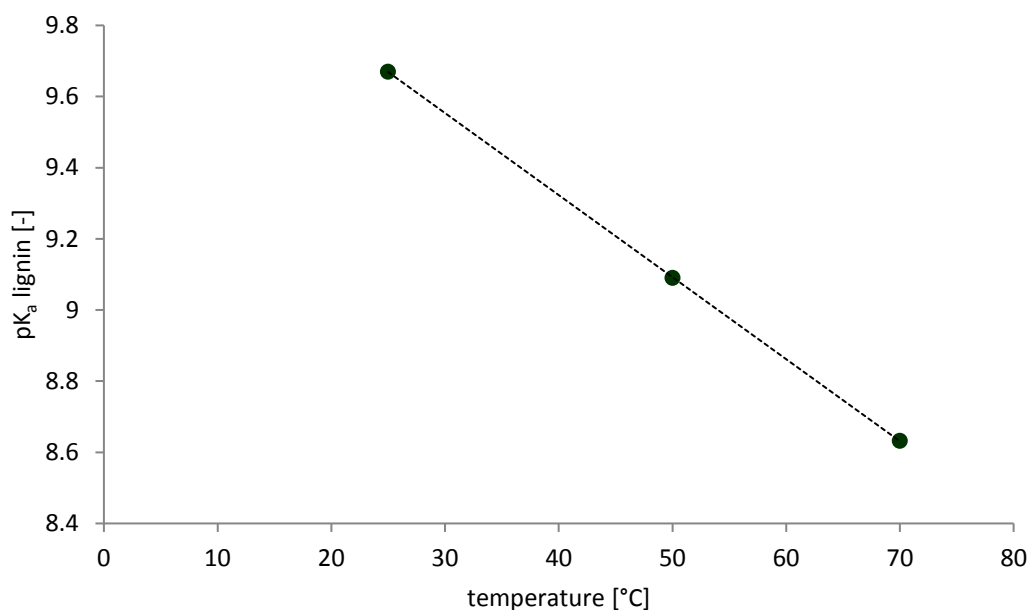
Figure 18. Plot of the estimated pK$_a$ of lignin Ph-OH groups at the three analysed temperatures. Green circles: average pK$_a$ from evaluation of the titration curves. Dashed line: fitted linear correlation, R^2=0.99998.

The average pK$_a$ of Ph-OH versu the titration temperature is plotted in Figure 18. In the analysed temperature range, there seems to be a perfectly linear relation between pK$_a$ and temperature, which facilitates the estimation of precipitation behaviour during acidification of BL in dependence on the temperature.

At a pH around 8 and lower, the titration curves converged and show similar pH values despite the large temperature difference. The reasons are most likely the same as explained above, i.e. the lower temperature dependency of the pH at more acidic conditions and a lower variation of the pK$_a$. In the respective range, the buffering action of lignin Ph-OH decreases and other buffer compounds like H$_2$S and carboxylic acids are neutralized. A less distinct temperature dependency of the pK$_a$ values of these groups would explain the decreased variation of the titration curves in the lower pH range.
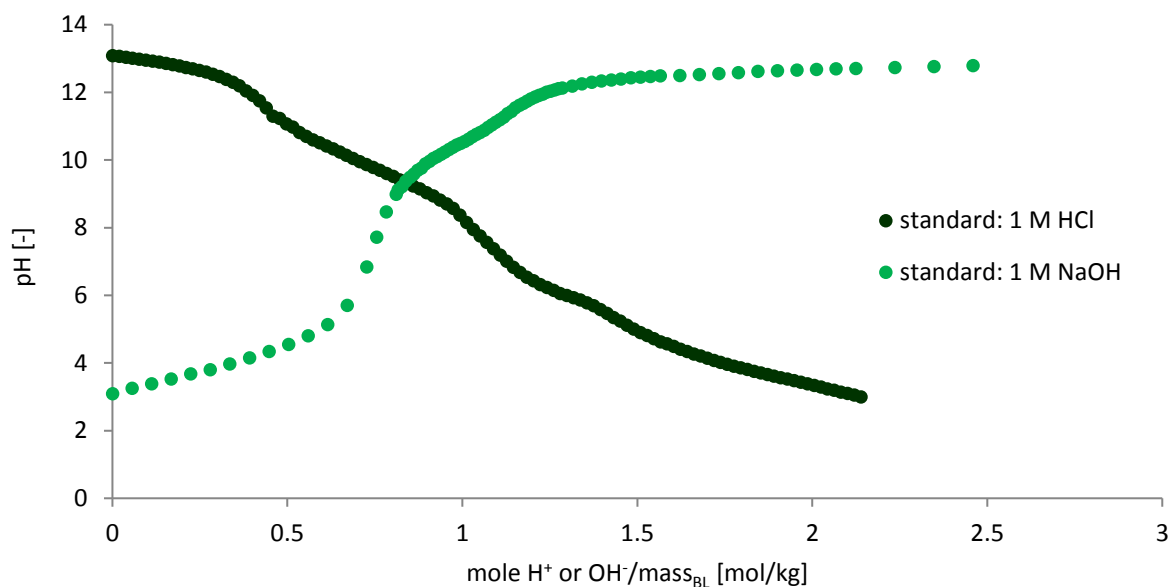
Figure 19. Titration curves of one BL sample, first with 1 M HCl to pH 3 (dark green circles), thereafter with 1 M NaOH until the initial pH was reached again (turquoise circles). Both experiments were performed at 25 °C.

Table 5. Estimated data resulting from the titration of one BL sample to pH 3 with 1 M HCl and back to pH 13 with 1 M NaOH.

	down-titration with HCl		up-titration with NaOH	
	pH	$mol_{HCl}/mass_{BL}$ [mol·kg^{-1}]	pH	$mol_{NaOH}/mass_{BL}$ [mol·kg^{-1}]
inflection point 1	11.54	0.44	11.44	0.75
inflection point 2	7.76	1.05	7.72	1.15
inflection point 3	5.76	1.43	-	-
pK$_a$ lignin	9.65	-	9.58	-
Ph-OH [mol·kg^{-1}]	5.00		3.24	

For one titration experiment, the BL was titrated with 1 M HCl until a pH of 3 was reached, then an aliquot of the resulting slurry was again titrated with 1 M NaOH until the pH was approx. 13 again. The resulting curves are plotted in Figure 19.

An analysis of concentrations and pK$_a$ values determined from these curves was performed, the results are summarized in Table 5. The concentration of Ph-OH groups and the lignin pK$_a$ for the first titration with HCl was in accordance with the results of the original experiments (see Table 4). However, even though the estimated pK$_a$ of 9.58 was similar, the back-titration with NaOH yielded different results for the Ph-OH content. With 3.24 mol·kg^{-1}, the concentration is significantly lower than the average value of 5.11 ± 0.21 mol·kg^{-1} determined previously. This difference indicates the Kraft lignin undergoes certain changes depending on the solution pH. A reduced Ph-OH content might indicate polymerisation or condensation reactions involving the phenolic groups. Another possibility is that the lignin does not completely re-dissolve after precipitation, which too would reduce the apparent concentration of Ph-OH found during titration.

The most prominent difference between the two curves in Figure 19 is the absence of any buffering reactions in the range of pH 5-9 in the back-titration curve. In this pH region, the dissolved hydrogen sulphide undergoes the reaction shown in Equation 28.

$$NaHS \ + \ H^+ \rightarrow H_2S \uparrow \ + Na^+$$

<div align="right">**Equation 28**</div>

The pK_a of H_2S is in the range of 7, although the exact value also depends on the ionic strength. When the solution pH approaches the pK_a of hydrogen sulphide, the formed dihydrogen sulphide is liberated to the gas phase due to its low solubility in the aqueous solution. This reaction drives the continuous loss of H_2S, which accelerates with decreasing pH values. Therefore, it is difficult to determine the pK_a and dissolved amount of sulphide by simple titration experiments. However, the absence of any buffering reactions in the relevant pH range of the up-titration curve shows, that the clear majority of H_2S has been liberated during the down-titration experiment, as is to be expected.

5.3   Precipitation experiments

5.3.1   Lab-scale precipitation

The primary goal of work package "Added-value lignin processing" of the FLIPPR[2] project is to develop and implement a pilot scale process for lignin precipitation from Kraft black liquor. Requirements for the process are that it has the smallest possible impact on the recovery cycle and balance of the pulp mill and to use flue gas from the site for acidification. The precipitation of lignin from Kraft black liquor has already been extensively studied and, as described in part 2, so far three major technologies have been implemented successfully. Parallel to the development of a pilot-scale reactor, precipitation of lignin on a small scale gave valuable insights for process development and design. The lab-scale experiments were performed in order to evaluate the practicability of the overall precipitation process based on literature data. Additionally the isolated lignin was used to carry out experiments concerning washing characteristics and solubility of the solid product.

The chosen temperature for all precipitation experiments was 70 °C corresponding to temperature ranges reported in the literature [26], [28], [42]. The CO_2 gas flowrate was set to 50 L·h^{-1}, similar to the 60 L·h^{-1} that were applied by Wallmo and coworkers, who reached a pH of 9 (at RT) within 20-30 min [30]. The final precipitation pH of 8.7-8.9 (at 70 °C) was chosen to assure high lignin yield as well as low precipitation time and little H_2S formation. This pH corresponded to a pH of approx. 9.7-10.0 when measured at room temperature. Although it has to be considered that all this literature data is only strictly valid for the black liquor and conditions chosen by the respective group, it still gives reasonable indications of feasible process conditions.

Table 6. Summary of the results of the lab-scale precipitation experiments. The final pH at 70 °C was measured instantaneously after acidification prior to ageing, the final pH at room temperature was measured mostly after storage of several days at 4 °C. The lignin concentration of the LLBL, $c_{Lignin,LLBL}$ was measured spectrophotometrically after several days of storage at 4 °C.
*not determined

Experiment	Start pH (70 °C)	Final pH (70 °C)	Final pH (25 °C)	Precipitation time [min] / BL feed [g]	$c_{Lignin,LLBL}$ [g·L^{-1}]
1	10.64	9.0	10.49	55 / 1056	54.5
2	n.d.*	8.68	9.93	60 / 1402	72.0
3	10.3	8.65	9.69	40 / 1099	58.2
4	10.3	8.75	9.91	60 / 1160	65.0

The relevant data for the lab-scale precipitation experiments are summarized in Table 6. In theory, there is a direct correlation between final precipitation pH – at 70 °C and at room temperature – precipitation time and lignin concentration in the residual lignin lean liquor. As can be seen from the data, this correlation only partially applies to the collected data. Espescially the results of experiment 1 are inconsistent and do not fit to the relations observed for the other three sets of data. The pH values measured in the course of this experiment are too high. This can be attributed to the inadequate calibration of the pH electrode. Considering the measured lignin concentration in the LLBL and the precipitation time, the final pH actually was most likely in the same range as after the other experiments. The results of experiments 2-4 show some correlation between final precipitation pH and the lignin concentration of the corresponding LLBL. The experiment 2 with the highest final pH of 9.93 (at RT) also had the highest residual lignin content of 72 g·L^{-1} in the LLBL. Experiment 3 with the lowest final pH (9.69 at RT) had the lowest residual lignin content of 58.2 g·L^{-1}. However, experiment 4 had a pH nearly equal to experiment 2 but still a considerably lower lignin content in the LLBL. Furthermore, the ratios between pH values measured at 70 °C directly following the acidification do not fit to those measured at room temperature. As there are many sources of possible errors for the pH measurement as well as the determination of UV-lignin, these variations can likely be attributed to such measurement incertainties. Some parameters affecting the pH measurement have already been discussed in part 5.1, but also the storage time and -conditions can influence the measured pH of LLBL, possibly due to liberation of gaseous H_2S or CO_2, as well as chemical reactions or precipitation of salts. Investigation of such effects has not been subject of this study, though. The lignin yield and thus remaining lignin content of LLBL mainly depends on the precipitation pH but also on many other factors like the precipitation conditions and black liquor used. For example a differing filtration temperature likely has an effect on lignin yield since the lignin solubility is temperature dependent. The particle size of precipitated lignin is e.g. depending on mixing conditions during acidification as well as ageing [55]; particles smaller than 4-12 µm would slip through the filter medium, at least prior to cake build-up. Such small particles and lignin precipitated after cooling/during storage of LLBL are still detected

partially during the UV-spectrophotometric measurement and introduce further variations due to possibly inadequate dispersion.

The precipitation time, which should be proportional to the amount of BL fed into the reactor, also strongly varies between the four experiments. The kinetics of CO_2-absorption are depending on the rheology and gas dispersion, which slightly varied between the different experiments and most likely contributed to the fluctuation of the required precipitation times. Insufficient gas dispersion and differing composition (solid content, buffer capacity) could also be responsible for the deviation of precipitation time compared to data published by Wallmo and coworkers. They reported an acidification time of approx. 10-15 min for 2 L of softwood BL using a gasflow of 1 L·min^{-1} pure CO_2 [30].

Experiment 4 was performed without any ageing step, except for the duration of the acidification, which itself took 60 minutes and thus could be considered a partial ageing towards the end. The ageing step was skipped because during the pilot-scale precipitation experiments proper ageing, as is employed in the LignoBoost as well as the LignoForce systems [28], [55], is not easily possible. The impact of the skipped ageing on the filtration was only qualitatively estimated in order to assure the applicability of precipitation without ageing. The resulting slurry was visually examined and then filtered. Throughout the procedure, no significant differences to the aged slurry and precipitate could be observed.

Evaluation of the lab-scale experiments confirmed the suitability of the chosen process conditions. A final pH of approx. 9 (at 70 °C) and precipitation without ageing gave, in a reasonably short time, an easily filterable lignin product in sufficient yield (see part 5.3.2.1).

5.3.2 Pilot-scale precipitation

The parameters of the pilot-scale precipitation experiments are summarized in Table 7. These experiments are described in much more detail by Andreas Pirschner in [62].

Table 7. Summary of the results of the pilot-scale precipitation experiments. The final pH at 70 °C was measured instantaneously after acidification, the final pH at room temperature was measured usually after storage of several days at 4 °C. The lignin concentration of the LLBL, $c_{Lignin,LLBL}$ was measured spectrophotometrically after several days of storage at 4 °C.

Experiment	Conditions	Start pH (70 °C)	Final pH (70 °C)	Final pH (25 °C)	Precipitation time [min] / BL feed [g]	$c_{Lignin,LLBL}$ [g·L^{-1}]
1_70/100	70 °C, 100 % CO_2	10.52	8.73	10.03	45 / 6010	n.A.
2_70/100	70 °C, 100 % CO_2	n.d.	9.08	10.95	30 / 4423	100.0
3_70/16	70 °C, 16 % CO_2	10.41	9.10	11.18	60 / 4313	107.2
4_70/100	70 °C, 100 % CO_2	10.25	9.10	10.62	21 / 4292	73.50
5_50/100	50 °C, 100 % CO_2	10.85	9.30	10.61	28 / 4382	58.65
6_70/16	70 °C, 16 % CO_2	10.31	9.10	11.08	80 / 4303	114.8

The acidified slurry obtained from experiment 1_70/100 was stored for one night at room temperature prior to filtration. This resulted in a hard-to-filter lignin slurry, the filter cake plugged almost immediately, leading to impracticable filtration velocities. Hence the slurry was diluted with about the same volume of hot (approx. 60 °C) water prior to filtration, which impeded the yield due to re-dissolution of lignin but facilitated recovery of the remaining solid. In consequence, the lignin concentration of the pure LLBL could not be determined and calculation of a lignin balance was rendered impossible. A reason for the bad filterability might have been further precipitation of very small lignin particles throughout cooling and storage. Such particles could have partially plugged the filter cake and hence increased the filter cake resistance. The addition of hot water to the slurry would have led to re-dissolution of such small particles, and therefore facilitated the filtration.

Throughout subsequent precipitation experiments, the slurry was always filtered when still at 40-50 °C to ensure sufficient filterability.

5.3.2.1   *Mass balance*

To evaluate the precipitation system, a lignin mass balance was calculated for all experiments where sufficient data had been collected. The balance is based on the masses of the product fractions, corresponding DS content and UV-lignin in the Feed and LLBL.

The mass of solid precipitated lignin in the isolated filter cake can be calculated from the DS contents of filter cake and LLBL under the assumption that all solid precipitate in the product slurry consisted of pure lignin. In praxis, the cake might also contain other solids like fibres originating from the BL or

complexes of lignin and hemicellulose. The mass of lignin and LLBL in the filter cake is given by Equation 29 and Equation 30.

$$m_{LLBL,c} = \frac{\left(1 - \frac{DS_c}{100}\right) \cdot m_c}{\left(1 - \frac{DS_{LLBL}}{100}\right)}$$

Equation 29

$$m_{lignin,c} = m_c - m_{LLBL,c}$$

Equation 30

With

- $m_{LLBL,c}$: mass of LLBL in the original filter cake [g]
- DS_c: solids content of the original filter cake [%]
- DS_{LLBL}: solids content of the LLBL [%]
- m_c: total mass of original filter cake [g]
- $m_{lignin,c}$: mass of lignin in the original filter cake [g]

The UV-lignin was calculated based on Lambert-Beer's law (Equation 31):

$$c_{lignin} = f \cdot \frac{Abs}{d \cdot \varepsilon}$$

Equation 31

With

- c_{lignin}: concentration of lignin in the original BL or LLBL sample [g·L^{-1}]
- Abs: measured absorbance [-]
- d: path length of light, here 1 cm [cm]
- ε: extinction coefficient of lignin [L·g^{-1}·cm^{-1}]
- f: dilution factor of measured sample [-]

The difference between lignin mass in the BL feed and the sum of isolated lignin in the cake and dissolved lignin remaining in the LLBL was calculated according to Equation 32 and Equation 33.

$$\Delta m_{lignin} = c_{lignin,BL} \cdot \left(\frac{m_{LLBL} + m_c}{\rho_{BL}}\right) - m_{lignin,c} + \left(\frac{m_{LLBL} + m_{LLBL,c}}{\rho_{LLBL}}\right) \cdot c_{lignin,LLBL}$$

Equation 32

$$error \; [\%] = 100 \cdot \frac{\Delta m_{lignin}}{c_{lignin,BL} \cdot \left(\frac{m_{LLBL} + m_c}{\rho_{BL}}\right)}$$

Equation 33

With

- $c_{lignin,BL}$: concentration of lignin in the feed BL [g·L^{-1}]
- Δm_{lignin}: difference in lignin mass resulting from mass balance [g]
- m_{LLBL}: total mass of original LLBL filtrate [g]
- ρ_{BL}: density of BL at 25 °C [g·L^{-1}]
- $c_{lignin,LLBL}$: concentration of lignin in LLBL [g·L^{-1}]
- ρ_{LLBL}: density of LLBL at 25 °C [g·L^{-1}]
- $error$: deviation of balance related to input mass of lignin [%]

The raw data and intermediate results for the mass balance are summarized in Table 16 in the appendix. The final results are shown in Table 8.

Table 8. Results of the calculated lignin mass balances. For pilot-scale experiments 5 and 6 only a representative part of the slurry was filtered for balancing. Therefore, the measured absolute masses for the various fractions are only smaller fractions, but the actual error and the lignin yield are not influenced by this procedure.

Experiment	$m_{lignin,c}$ [g]	$m_{lignin,BL}$ [g]	$m_{lignin,LLBL}$ [g]	Δm_{lignin} [g]	error [%]
2_70/100	121.3	523.1	352.0	49.80	9.52
3_70/16	67.19	512.8	376.7	68.88	13.43
4_70/100	196.2	510.9	249.4	65.33	12.79
5_50/100	4.04	9.32	3.61	1.67	17.89
6_70/16	27.01	149.4	116.2	6.27	4.19
lab-scale #1	57.40	117.0	43.86	15.73	13.45

For the balance, deviations due to losses of slurry in the reactor and filter equipment were not included. This was assured by taking the sum of LLBL- and filter cake mass also as the BL feed mass (see Equation 32). In truth, typically around 1 % of the BL feed mass were lost due to residual material in the precipitation and filtration equipment. Furthermore, the diluting effect of CO_2 absorption into the slurry was not taken into account.
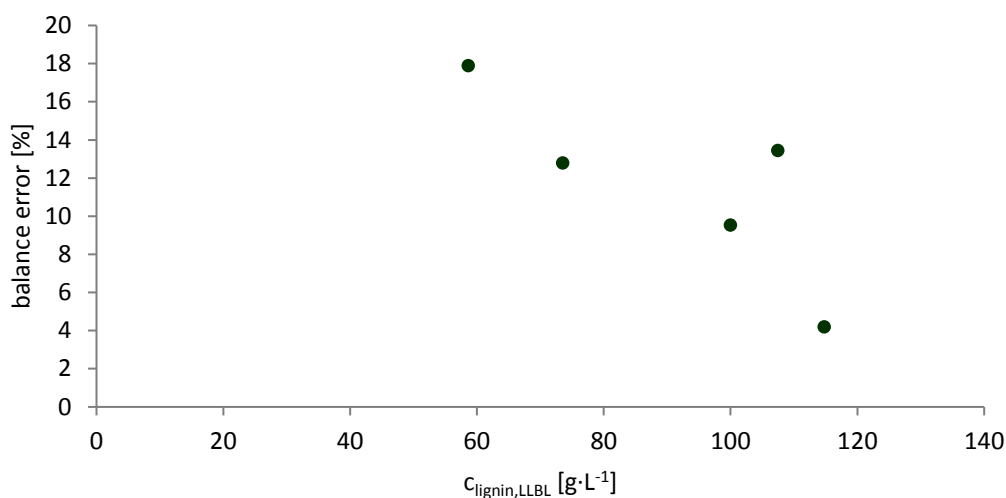
Figure 20. Plot of the balance error versus the residual lignin in the LLBL. The values correspond to pilot-scale precipitation experiments 2-6. The lignin concentration in the LLBL was measured with UV-VIS spectrophotometry.

As can be seen from the data summarized in Table 8 and the corresponding plot (Figure 20), the relative error of the lignin balance calculation is generally high. Furthermore, the plot clearly shows a trend to increasing error with decreasing lignin concentration in the corresponding LLBL. Part of this error can be attributed to the fact that the slurry residue in the precipitation device and transfer vessels consists of a disproportionally high amount of solid lignin. This leads to a general underestimation of lignin yield and a higher error. The long storage time of LLBL prior to absorbance measurements could also have had an influence on the measured values due to ageing reactions in the LLBL. A more likely explanation for the observed relation between error and lignin content in the LLBL is the UV-VIS absorbance

method applied for lignin quantification. It has been found that the extinction coefficient which relates absorbance to concentration is strongly dependent on the lignin source, processing and pH [67], [68]. It is also known that the lignin fractions having higher molar masses precipitate first during acid precipitation, which means that with increasing precipitation yield and decreasing pH the average molar mass of the lignin dissolved in the LLBL decreases. If the extinction coefficient of lignin decreases with decreasing molecular weight, this explains the clear correlation seen in Figure 20. Such a deviation would also indicate that the evaluation of the UV-lignin content is not suitable for balancing as long as the extinction coefficient is not adapted for lignin of lower molecular mass.

The corresponding data pair of the lab-scale precipitation experiment 1_70/100 is not plotted in Figure 20, but the data show that the trend observed for the pilot-scale precipitation applies here, too. The observed error is not as high as the one of pilot-scale precipitation experiment 5_50/100 (of which the UV-lignin in the LLBL was almost equal) because the lab-scale precipitation required less transfer steps and the corresponding loss of solid lignin was comparably lower.

The only data pair that clearly deviates from the general trend is that of pilot-scale precipitation 3_70/16. The lignin yield (see below) is also much lower than would be expected from the residual UV-lignin in the corresponding LLBL. The reason for this deviation is not entirely clear yet, possibly it is simply due to an error during weighing of the filter cake.

The total yield of dry lignin was calculated based on Equation 34. The corresponding percentage of lignin recovered from the initial amount of lignin dissolved in the feed BL (based on the UV-lignin content) was calculated from Equation 35. For the yield losses due to material residues remaining in the equipment are included by relating the product mass to the total input mass of BL.

$$Y = \frac{m_{lignin,c}}{m_{BL}}$$

<div align="right">**Equation 34**</div>

With
- Y: yield of lignin based on the BL feed [g·kg^{-1}]
- m_{BL}: total input mass of BL [kg]

$$recovery = \frac{m_{lignin,c}}{m_{lignin,BL}} \cdot 100$$

<div align="right">**Equation 35**</div>

With
- $recovery$: yield of lignin based on initial amount of lignin dissolved in feed BL [%]

The yield of pure lignin for the different precipitation experiments is summarized in Table 9. Figure 21 shows that the yield roughly correlates with the amount of dissolved lignin in the residual LLBL, as is to be expected. As discussed for the error of the lignin balance, the results of lab-scale precipitation 1 also fit to the trend and the precipitation experiment 3_70/16 is a clear outlier. As already mentioned

above, the plot in Figure 21 has to be regarded with precaution, since the UV-lignin measurement might underestimate the actual amount of dissolved lignin, especially for lower concentrations.

Table 9. Calculated lignin yield and recovery.

Experiment	Yield [g lignin·(kg BL)$^{-1}$]	Recovery [%]
2_70/100	27.4	19.0
3_70/16	15.6	10.8
4_70/100	45.7	31.7
5_50/100	51.5	35.7
6_70/16	22.7	15.8
lab-scale #1	54.4	37.7
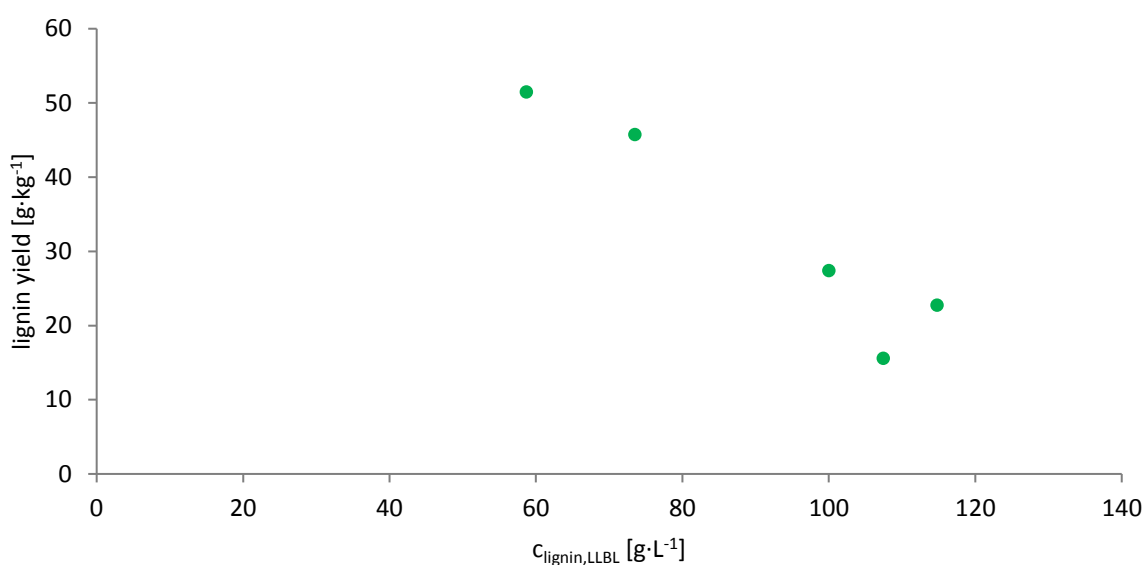
Figure 21. Lignin yield versus residual lignin in the corresponding LLBL. The yield was related to the initial mass of BL. The values correspond to pilot-scale precipitation experiments 2-6. The lignin concentration in the LLBL was measured with UV-VIS spectrophotometry.

The highest lignin yield of the pilot-scale experiments is with 51.5 g·kg^{-1} still low compared to values published in the literature, where the reported yield usually lies in the range of 60 % of total lignin. Based on the UV-lignin content of the feed BL, 51.5 g·kg^{-1} correspond to precipitation of 35.7 % of total lignin. This deviation is mainly caused by the high precipitation pH chosen for these experiments. A large portion of lignin precipitates between pH 10 and 9, but the experiments discussed in this thesis were usually stopped at a pH of 10-10.5 in order to prevent excessive formation of toxic H$_2$S. A lower precipitation pH would also significantly increase the lignin yield.

5.3.2.2   *Filter cake resistance*

The filter cake resistance of the lignin precipitate generated throughout experiments 3-6 was determined based on the Darcy equation for constant pressure drop. One representative example of the thereby generated data sets is shown in Table 10, all the other data can be found in Table 17-Table

20 in the appendix. The corresponding plots in Figure 22 and Figure 23 show the increase of total filtrate volume over time and the linear plot for constant pressure according to Equation 20, respectively.

Table 10. Exemplary data of the filter cake resistance measurement for experiment 4_70/100.

t [s]	V [m³]	t/V [s·m⁻³]
9.67	$5 \cdot 10^{-6}$	$1.93 \cdot 10^{6}$
21.38	$1 \cdot 10^{-5}$	$2.14 \cdot 10^{6}$
36.87	$1.5 \cdot 10^{-5}$	$2.46 \cdot 10^{6}$
51.16	$2 \cdot 10^{-5}$	$2.56 \cdot 10^{6}$
68.8	$2.5 \cdot 10^{-5}$	$2.75 \cdot 10^{6}$
89.62	$3 \cdot 10^{-5}$	$2.99 \cdot 10^{6}$
110.16	$3.5 \cdot 10^{-5}$	$3.15 \cdot 10^{6}$
133.62	$4 \cdot 10^{-5}$	$3.34 \cdot 10^{6}$
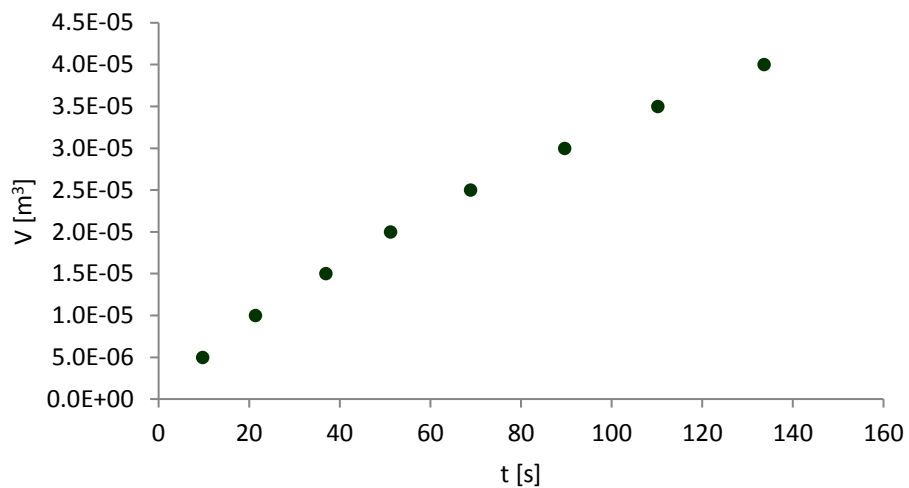
Figure 22. Increase of filtrate volume over time, recorded for the determination of filter cake resistance of the lignin cake generated in experiment 4_70/100.
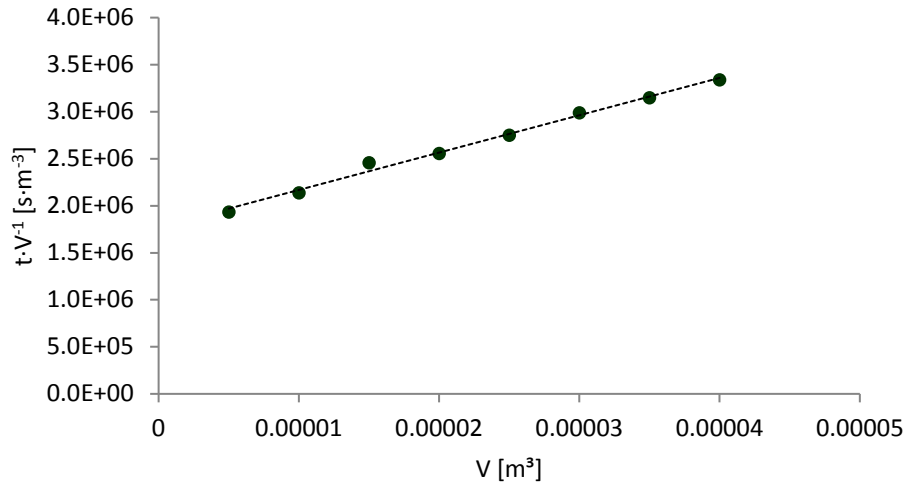
Figure 23. Linear plot according to Equation 20 for the data set of experiment 4_70/100 shown in Table 10 and Figure 22. The black dashed line gives the fitted linear correlation, R²=0.9929.

From the slope of the linear plot, the average filter cake resistance was determined according to Equation 22. The resistance β of the filter media was determined from the corresponding intercept of the linear equation. For the example plotted in Figure 23, the linear equation is

$$\frac{t}{V} = V \cdot 3.97 \cdot 10^{10} + 1.77 \cdot 10^{6}$$

Equation 36

The calculated average resistances are summarized in Table 11. The corresponding data is summarized in Table 21 and Table 22 in the appendix.

Table 11. Resulting resistances determined for the lignin filter cake and filter media.

Experiment	β [m⁻¹]	αH [m⁻²]	αM [m·kg⁻¹]
3_70/16	$1.08 \cdot 10^{10}$	$2.43 \cdot 10^{12}$	$3.14 \cdot 10^{10}$
4_70/100	$1.36 \cdot 10^{10}$	$2.41 \cdot 10^{12}$	$1.59 \cdot 10^{10}$
5_50/100	$1.61 \cdot 10^{10}$	$1.30 \cdot 10^{13}$	$1.31 \cdot 10^{11}$
6_70/16	$4.70 \cdot 10^{9}$	$4.05 \cdot 10^{12}$	$4.70 \cdot 10^{10}$

The resistance of the filter media (β) is much lower than that of the filter cake, which means that the media resistance does not contribute considerably to the overall pressure drop, as is often the case. The standard deviation of the filter media resistance determined for each experiment was with 15-40 % very high (data not shown). In comparison, the standard deviations of filter cake resistances were between 5 and 15 %. The measurement of the resistances relied on the visual observation of the filtrate volume in a graduated cylinder where a continuous stream of filtrate was dripping on the liquid surface, rendering the exact determination of filtrate volume difficult. Furthermore, the slurry had to be added to the funnel regularly to keep the liquid level approximately constant. Another source of variation was the fluctuation of underpressure applied by the vacuum pump, which varied in the range of 10 Pa. The start of filtration time strongly influenced the calculated filter media resistance, which is

the resistance at "time 0", where no filter cake was formed yet. Thus, slight variations of the starting time are responsible for the high standard deviation of the calculated filter media resistances.

The plot in Figure 23 shows that the relation between t/V and V is not exactly linear. The dent visible between the third and fourth data point is present in all the experiments to a certain extend. It is most likely caused by sedimentation of larger particles in the slurry after it has been poured into the Buchner funnel. If larger particles sediment before the corresponding portion of liquid reaches the surface of the cake, while smaller particles remain suspended, a curve shaped similar to that in Figure 23 can be observed [59]. This further contributes to the variation of the resulting resistances depending on the filtration speed and thus the solids content of the initial slurry.

The resistance α_M that is related to the solids load K_M was calculated based on the overall solids load in the slurry. The resistance α_H on the other hand was based on K_V that was determined separately for each single measurement (the resistance of each slurry was determined in triplicate). This explains why the difference between α_H and α_M is not proportional for all experiments. The filtration properties of the experiments are compared based on α_H because the use of K_H and Equation 24 at least partially eliminates the bias caused by incomplete dispersion in the slurry sample. However, effects of segregation which influences cake porosity and overall filtration resistance could not be accounted for. It should be considered that larger particles did sediment faster in the original product slurry and where thus probably underrepresented in the resulting samples used for determination of filter cake resistances. This effect could be diminished by thorough shaking of the slurry prior to sampling, but it probably could not be prevented completely. Since larger particles usually improve the filtration properties, the filtration of the total slurry might yield better results than the filter cake resistance determined here indicates.

The influence of the precipitation temperature on the filtration resistance is reflected by the strong difference in filter cake resistances of experiments 4_70/100 and 5_50/100, where all conditions were equal except for the temperature throughout acidification. Experiment 4_70/100 was carried out at 70 °C and has a filter cake resistance of $2.41 \cdot 10^{12}$ m^{-2} compared to $1.30 \cdot 10^{13}$ m^{-2} measured for experiment 5_50/100 which was performed at 50 °C. The difference of a factor of nearly 10 can be attributed to different aggregation and precipitation characteristics of lignin which influences the filtration properties. These results are consistent with the literature, where acidification temperatures of up to 85 °C are recommended [26].

The filter cake resistance of experiment 3_70/16, which was carried out at 70 °C with dilute CO_2 is in the same range as that of experiment 4_70/100. Experiment 6_70/16 was also carried out with dilute CO_2, but the filter cake resistance is higher than for the other two 70 °C experiments. The only

difference between experiment 3_70/16 and 6_70/16 is a higher gas flow rate and, resulting from this, a shorter acidification time for experiment 3_70/16 compared to experiment 6_70/16 (during experiment 3_70/16, the gas flow rate was around 300 L·h^{-1}, while it was only 230 L·h^{-1} for experiment 6_70/16). Therefore, one or both of these factors have a considerable influence on the filtration properties of the lignin product, though the effect is by far not as pronounced as for the acidification temperature.

Compared to values published in the literature, the filtration properties are in the average range. Ohman et.al. published resistances between $1 \cdot 10^{10}$ and $1 \cdot 10^{13}$ m·kg^{-1} for the lignin produced by the LignoBoost system [28]. Kannangara et.al. reported filter cake resistances of LignoForce lignin precipitated under different mixing conditions. In the best case, the measured resistance was around $2 \cdot 10^{9}$ m·kg^{-1}, while deviating mixing and ageing conditions gave filter cake resistances in the range of $8 \cdot 10^{9}$ and $3 \cdot 10^{11}$ m·kg^{-1} [55]. Considering that an ageing step for the slurries produced by experiments 3-6 was not possible, the resulting filter cake resistances are very good.

5.4   Lignin solubility

5.4.1   Suspension time

Three aliquots of filter cake (around 100 g each) were suspended with an equal mass of water (RT) and incubated for 1, 10 and 42 minutes. The resulting lignin concentrations in the liquid phase are summarized in Table 12 and plotted in Figure 24.

Table 12. Lignin concentration in filtrate depending on the incubation time.
Dissolution experiments were performed at room temperature and mixing of 200 rpm.

Incubation time [min]	Lignin concentration [g·L^{-1}]
1	32.12
10	39.84
42	46.42
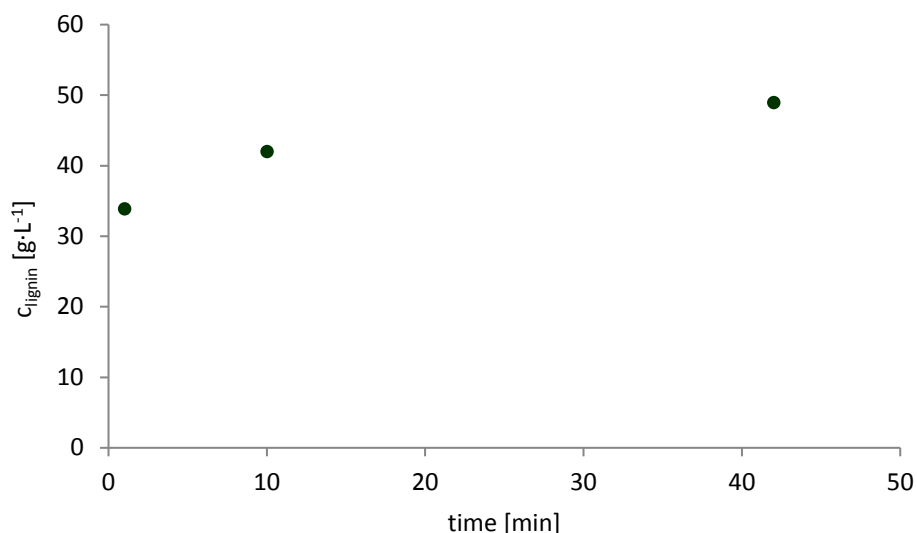
Figure 24. Plot of lignin concentration in filtrate depending on the incubation time. Dissolution experiments were performed at room temperature and mixing of 200 rpm.

The solubility of precipitated lignin is clearly depending on the resuspension time, as can be seen in Figure 24. After 10 min of incubation, the equilibrium concentration had not been reached but the dissolution rate slowed down considerably. Further experiments would be necessary to evaluate the exact time needed for equilibrium to be established.

5.4.2   Solids concentration

In order to evaluate the influence of filter cake concentration on lignin solubility, filter cake aliquots were re-suspended with 1x, 2x and 5x the mass of H_2O and then incubated for 10 minutes each. It has to be considered that the unwashed and wet filter cake contained around 2/3 of mother liquor (LLBL) and that the mother liquor had a UV-lignin concentration of about 72 $g \cdot L^{-1}$.

The lignin concentrations in the resulting filtrates are summarized in Table 13.

Table 13. Lignin concentration in filtrate depending on the cake : water ratio. Dissolution experiments were performed at room temperature and mixing of 200 rpm.

Resuspension (parts filter cake : parts H_2O)	Lignin concentration [$g \cdot L^{-1}$]
1:1	46.42
1:2	35.32
1:5	26.81

Other than for part 5.4.1 where the contribution of the lignin-lean liquor to the lignin concentration in the resuspension filtrate was constant (constant dilution factor), the concentration of lignin introduced by the LLBL is depending on the ration of filter cake to water added. If it is assumed that the initial filter cake contains 33 % solid lignin and 67 % LLBL, the results can be adjusted to take into account this additional lignin. Firstly, the ratio of liquid phase to solid phase can be calculated. The results are shown

in Table 14. From the concentration and the amount of liquid the theoretical mass of dissolved lignin per equivalent of solid filter cake can be calculated according to Equation 37 and plotted against the dilution (Figure 25).

$$m_{lignin,dis.} = liquid:solid\ ratio \cdot c_{lignin}$$

Equation 37

With

- $m_{lignin,dis.}$: theoretical mass of dissolved lignin [g]
- $liquid:solid\ ratio$: ratio of liquid consisting of added water and LLBL from the filter cake to solids in the filter cake [-]
- c_{lignin}: lignin concentration in the filtrate after incubation [g·L^{-1}]

Table 14. Dissolved lignin mass per equivalent of solid lignin from the filter cake depending on the liquid : solid ratio.

Resuspension (parts liquid : parts solid lignin)	Dissolved lignin [g]
5:1	232
8:1	283
17:1	456
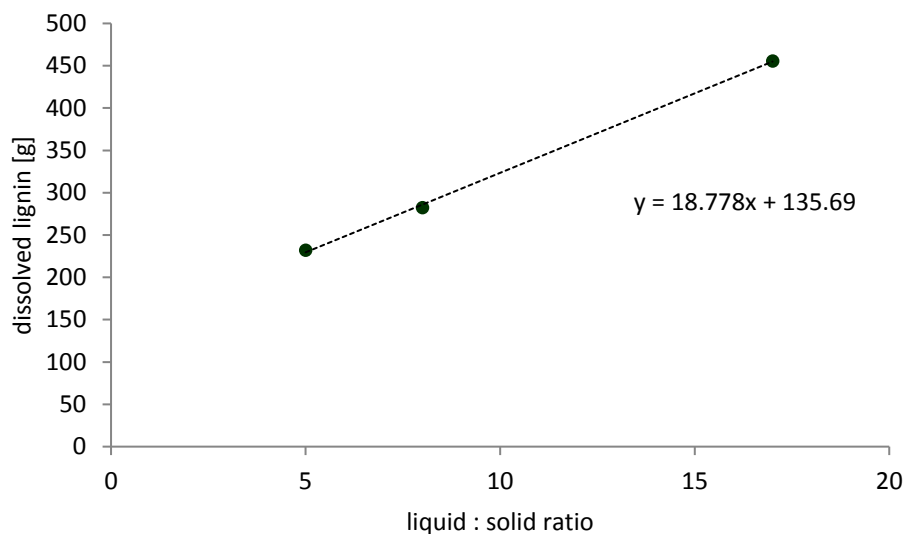
Figure 25. Theoretical dissolved mass of lignin per equivalent of filter cake, depending on the liquid : solid ratio. The black dashed line gives the fitted linear correlation, R^2=0.9998.

The plotted results show a highly linear correlation between amount of liquid and dissolved mass of lignin, which means that in all three samples the dissolved concentration of lignin was the same. From the linear equation describing the correlation, two things can be deduced: First of all, the concentration of lignin in the lignin lean black liquor can be estimated from the intercept. This value corresponds to the amount of lignin present in the solution independently of the amount of additional liquid added. Hence, 135.69 g of lignin were extracted from the wet lignin cake, which corresponds to two

equivalents of LLBL based on one equivalent of solid lignin (because we assumed that 2/3 of the cake consisted of LLBL). Divided by two, this gives 68 g lignin per equivalent of liquid, therefore 68 g·L^{-1} lignin in the LLBL. This fits very well to the amount of 72 g·L^{-1} found with the UV absorbance measurements of the LLBL present in the initial filter cake. The slope of the linear equation then equals the amount of lignin dissolved per equivalent of liquid, thus 18.8 g·L^{-1}. According to these experiments, the absolute solubility of the precipitated lignin during 10 min of suspension at RT is 18.8 g lignin per L of pure water. Furthermore, these results imply that the lignin dissolution is not significantly influenced by the ionic strength, at least not in the evaluated range. The ionic strength was highest in the 1:1 sample and lowest in the 1:5 sample, but the concentration of additional lignin dissolved was similar in all three samples. Additionally, it seems that the lignin dissolution of precipitated lignin is not influenced by the residual amount of lignin present in the LLBL.

For evaluation of these results it has to be considered, that the uncertainty is very high. First of all, the samples were not incubated until equilibrium was reached but only for 10 minutes, thus dissolution rate might also have had an influence on the results. Furthermore, the basis for solid : liquid ratio and the subsequent calculations was the assumption that the density of all constituents is similar, even though there surely are certain differences. Although these solubility estimations might be biased, they can serve as a basis for further experiments and give a general guideline for application of aqueous lignin solutions. One of the considered options for further treatment of precipitated lignin was to re-dissolve the precipitate in water and then purify it by means of membrane operations like ultrafiltration. However, the estimated lignin solubility is so low that ultrafiltration would lead to precipitation of lignin on the membrane surface, which renders this option impractical.

5.4.3   Solvent pH

The influence of the solvent pH on the lignin solubility was estimated in one experiment. An aliquot of unwashed filter cake was suspended in the same amount of either pure water or NaOH solution at pH 10. The pH and the UV-lignin content in the filtrate were measured after 10 min of resuspension at 40 °C, the results are shown in Table 15.

Table 15. Resulting final pH values and UV-lignin concentrations of the dissolution samples.

Solvent	pH (40 °C) [-]	Lignin concentration [g·L^{-1}]
H$_2$O	10.31	57.5
NaOH solution, pH 10	10.30	56.2

The resulting lignin concentrations clearly show that the different solvent does not influence the solubility. Furthermore, the final pH of both solutions is the same, although the pH of the pure solvents is different. This implies that the pH after resuspension of the cake is determined by the residual LLBL in the cake or by the re-dissolved lignin, which acts like a buffer due to the partially protonated Ph-OH

groups. For further investigation of the solubility in dependence on the solvent pH, pure lignin with the least possible amount of residual LLBL and a buffer as solvent should be used. However, then it needs to be considered that the buffer capacity of the solvent depends on the ionic strength, which in turn might influence the lignin solubility.

6   Conclusion and outlook

Isolation of lignin from Kraft black liquor by acidification with CO_2 is a convenient way to reduce the recovery boiler load and to yield a high-potential raw material. An extensive literature review on Kraft lignin isolation revealed feasible ranges for process conditions like precipitation temperature, final pH and solids content of the initial black liquor.

The black liquor used for all experiments was provided by a local Kraft pulp mill. Characterization by titration experiments gave estimates for the lignin pK_a in dependence on the temperature and the total content of lignin Ph-OH groups. The average pK_a measured at 25 °C titration temperature was 9.67. At 70 °C, which was the actual precipitation temperature, it was with 8.63 significantly lower. In the range of 25-70 °C, the pK_a of lignin Ph-OH groups correlated linearly with the temperature. The concentration of Ph-OH groups in lignin was determined to be 5.11 mol kg^{-1}.

The first lab-scale precipitation experiments were designed based on the conditions identified throughout the preliminary literature study. The precipitation was carried out with black liquor of 32 % DS content at 70 °C and atmospheric pressure with pure CO_2 until a final pH of around 9.5 (at RT) was reached. These preliminary experiments could be performed without any major problems and gave very promising results. Subsequently, black liquor acidification followed by isolation of precipitated lignin on larger scale was successfully completed under similar conditions.

The application of dilute instead of pure CO_2 gas led to no major disadvantages or problems during precipitation and isolation of lignin, which is a very important result with regard to the application of flue gas for black liquor acidification. The gas was diluted with N_2 to a final CO_2 concentration of 16 % in the feed. The filterability of the lignin product was generally good, the filter cake resistance was in the range of 2.4-4·10^{12} m^{-2}. In one experiment, where black liquor was acidified at 50 instead of 70 °C, the resulting resistance was higher by nearly an order of magnitude, which proofs the importance of correctly adjusted process parameters.

Lignin mass balances showed that 16-52 g lignin per kg black liquor were precipitated under the applied process conditions. This corresponds to isolation of 11-37 % of the total lignin dissolved in the initial black liquor. A higher yield, as is often reported in the literature, can be achieved by further acidification to a lower final pH, e.g. in the range of pH 9 (at RT). However, a lower pH also leads to increased H_2S emissions, which still poses a problem during lab-scale experiments. Furthermore, the large error of the lignin balance in the range of 4-18 % implies that the applied analytical methods need to be improved.

A rough estimation of the lignin solubility in water indicated that purification of aqueous lignin solutions with membrane processes is not suitable due to the low solubility in the range of 20 g·L^{-1}. Further solubility studies investigating the effect of solvent compositions, temperature and time are required before lignin dissolution can be described more accurately.

7 List of literature

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10 List of Abbreviations

10.1 General

A^-	Conjugate base of acid HA
B^+	Conjugate acid of base BOH
BOH	Base
DS	Solids content
HA	Acid
M	Molar, $mol \cdot L^{-1}$
Ph-OH	Lignin phenolic OH-groups
SLRP	Sequential liquid-lignin recovery and purification process
TRS	Totally reduced sulphur

10.2 Symbols

c	$[mol \cdot m^{-3}]$ / $[mol \cdot kg^{-1}]$ $[g \cdot kg^{-1}]$ / $[g \cdot m^{-3}]$	Concentration
Δp	$[Pa]$	Pressure drop
A	$[m^2]$	Filter area
H	$[m]$	Filter cake height
η	$[Pa \cdot s]$	Dynamic filtrate viscosity
α_H	$[m^{-2}]$	Specific filter cake resistance
$\dot{V}$	$[m^3 \cdot s^{-1}]$	Filtrate flow rate
β	$[m^{-1}]$	resistance of the filter medium
V	$[m^3]$	Volume
K_H	$[-]$	Filter cake volume per filtrate volume
t	$[s]$	Filtration time
α_M	$[m \cdot kg^{-1}]$	Specific filter cake resistance
m	$[kg]$	Mass
a		Slope of integrated Darcy equation for constant pressure drop
b		Intercept of integrated Darcy equation for constant pressure drop
K_w	$[mol^2 \cdot L^{-2}]$	Equilibrium constant of water
K_M	$[kg \cdot m^{-3}]$	Solids load of feed suspension
$[H_3O^+]$	$[mol \cdot L^{-1}]$	concentration of H_3O^+ ions

$[OH^-]$	[mol·L⁻¹]	concentration of OH⁻ ions
K_a	[mol·L⁻¹]	equilibrium constant of acid HA
$[A^-]$	[mol·L⁻¹]	concentration of conjugate base of acid HA
$[HA]$	[mol·L⁻¹]	concentration of un-dissociated acid HA
Y	[g·kg⁻¹]	yield of lignin based on the BL feed
n_{H^+}	[mol]	moles of hydrogen ions required to acidify BL to final pH
ρ	[kg·m⁻³]	Density
Abs	[-]	Measured absorbance
d	[cm]	Path length of light
ε	[L·g⁻¹·cm⁻¹]	Extinciton coefficient of lignin
f	[-]	dilution factor of measured sample
Δm_{lignin}	[g]	Difference in lignin mass resulting from mass balance
$error$	[%]	deviation of balance related to input mass of lignin
m_{out}	[g]	mass of dry sample and crucible after drying
m_{tara}	[g]	dry mass of crucible
m_0	[g]	wet sample mass

10.3 Indices

BL	Black liquor
c	Lignin filter cake
LLBL	Lignin-lean black liquor
Ph-OH	Lignin phenolic OH-groups
m	Filter medium
HCl	Hydrochloric acid
B	Base
ip1	Inflection point 1
ip2	Inflection point 2
lignin,dis	Dissolved lignin

11 Appendix

Mass balance data is shown in Table 16.

Table 16. Raw data and intermediate results for the lignin mass balances. For pilot-scale experiments 5 and 6 only a representative part of the slurry was filtered for balancing. Therefore, the measured absolute masses for the various fractions are only smaller fractions.

Experiment	m_c [g]	DS_c [%]	m_{LLBL} [g]	DS_{LLBL} [%]	$c_{Lignin,LLBL}$ [g·L^{-1}]
2	855.9	40.46	3430	30.63	100.0
3	637.5	39.74	3564	32.64	107.4
4	1366	37.80	2820	27.36	73.50
5	37.15	34.93	39.21	26.98	58.65
6	186.4	40.75	1038	30.71	114.8
lab-scale #1	325.4	40.69	633.1	27.98	57.69

Table 17-Table 20 give the raw data for all the filter cake resistance measurements. The corresponding intermediate and final results can be found in Table 21 and Table 22.

Table 17. Filtration resistance data experiment 3: Time and filtrate volume measured during experimental filter cake resistance determination. Measurement 1 and 2 depict the duplicate determination.

1		2	
t [s]	V [m³]	t [s]	V [m³]
5	0.000005	8.5	0.000005
9	0.00001	13	0.000008
15	0.000016	18	0.000011
21	0.00002	25	0.000015
28	0.000025	35	0.00002
36	0.00003	57	0.00003
42	0.000035	70	0.000035
50	0.00004	82	0.00004
57	0.000045	96	0.000045
66	0.00005		

Table 18. Filtration resistance data experiment 4: Time and filtrate volume measured during experimental filter cake resistance determination. Measurement 1, 2 and 3 depict the triplicate determination.

1		2		3	
t [s]	V [m³]	t [s]	V [m³]	t [s]	V [m³]
13	5	0.000005	5	9.28	0.000005
24	10	0.00001	10	21.71	0.00001
38	15	0.000015	15	39.24	0.000015
55	20	0.00002	20	55.23	0.00002
75	25	0.000025	25	75.82	0.000025
96	30	0.00003	30	95.62	0.00003
118	35	0.000035	35	116.97	0.000035
				144.41	0.00004

Table 19. Filtration resistance data experiment 5: Time and filtrate volume measured during experimental filter cake resistance determination. Measurement 1, 2 and 3 depict the triplicate determination.

1		2		3	
t [s]	V [m³]	t [s]	V [m³]	t [s]	V [m³]
21.68	0.000005	21.44	0.000005	18.8	0.000005
59.7	0.00001	62.3	0.00001	53.64	0.00001
114.4	0.000015	127.08	0.000015	117	0.000015
176.77	0.00002	197.4	0.00002	190.04	0.00002
257.7	0.000025	283.68	0.000025	297.94	0.000025
352.16	0.00003	392.66	0.00003		

Table 20. Filtration resistance data experiment 6: Time and filtrate volume measured during experimental filter cake resistance determination. Measurement 1, 2 and 3 depict the triplicate determination.

1		2		3	
t [s]	V [m³]	t [s]	V [m³]	t [s]	V [m³]
7.23	0.000005	5.78	0.000005	6	0.000005
16.98	0.00001	14.99	0.00001	15.63	0.00001
30.48	0.000015	28.69	0.000015	33.61	0.000015
46.33	0.00002	41.45	0.00002	50.39	0.00002
61.34	0.000025	56.5	0.000025	71.29	0.000025
79.73	0.00003	72.05	0.00003	91.33	0.00003
97.25	0.000035	89.67	0.000035	114.77	0.000035
117.28	0.00004				

Table 21. Intermediate results and conditions of the filter cake resistance measurements.

experiment		Temperature [°C]	Δp [Pa]	η [Pa·s]	V_t [m³]	K_H [-]
3	1	48	11600	0.0028284	75.0	0.248
	2	35	9200	0.0038439	63.0	0.248
4	1	43	7700	0.0026536	50.5	0.618
	2	36	7200	0.0031644	50.0	0.654
	3	29	7200	0.0038438	44.0	0.726
5	1	34	7700	0.0030897	42.0	1.026
	2	27	7700	0.0037581	44.5	1.001
	3	25	7700	0.003988	34.0	1.005
6	1	36	7200	0.0046694	62.0	0.287
	2	33	7200	0.0051171	57.0	0.313
	3	28	7200	0.0060128	59.0	0.327

Table 22. Results of the filter cake resistance measurements.

experiment		slope a	intercept b	β [m^{-1}]	α_H [m^{-2}]	α_M [m·kg^{-1}]
3	1	9.15E+09	8.72E+05	1.06E+10	2.68E+12	3.46E+10
	2	1.28E+10	1.53E+06	1.09E+10	2.19E+12	2.83E+10
4	1	3.13E+10	2.21E+06	1.91E+10	2.59E+12	1.60E+10
	2	2.93E+10	2.24E+06	1.51E+10	1.80E+12	1.59E+10
	3	4.79E+10	1.74E+06	9.71E+09	2.18E+12	1.58E+10
5	1	2.93E+11	3.01E+06	2.23E+10	1.26E+13	1.29E+11
	2	3.47E+11	2.81E+06	1.71E+10	1.25E+13	1.26E+11
	3	4.09E+11	1.53E+06	8.79E+09	1.39E+13	1.39E+11
6	1	4.24E+10	1.33E+06	6.11E+09	4.02E+12	4.33E+10
	2	4.55E+10	1.07E+06	4.47E+09	3.61E+12	4.23E+10
	3	7.01E+10	9.84E+05	3.50E+09	4.53E+12	5.55E+10