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Comparison of FBRM® and PIA for investigating the precipitation of Kraft lignin from aqueous solutions: Influence of salt type, concentration, temperature and pH

Master's Thesis-Chemistry and Chemical Engineering

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Abstract

In this work, precipitation of softwood Kraft lignin was studied. Two methods for measuring the particle size distribution were used and compared to each other. The first method has been successfully used in other studies and is called FBRM® (focused beam reflectance measurement), which is a laser-based light technique. The other is a new optical measuring method referred to as particle size analyzer or PIA. The experimental parameters in this study was temperature, pH, lignin concentration, salt type and concentration. FBRM® measurements were done *in situ* in order to gain further understanding of the precipitation. The effect of salt addition beyond the amount needed for onset of precipitation has also been studied. The study has been focused on commissioning the PIA-equipment, development of the PIAs experimental method and analysis of its performance. Analyzing the PIA was done by comparing the volume based particle size distribution from it with a calculated volume based particle size distribution from the FBRM® results. The chord length distribution from the FBRM® was extremely consistent in between all the experiments with the only truly deviating result coming from a single experiment. The deviating result came from an experiment at room temperature where the solution underwent gelation. Adding additional salt increased the chord counts but did not change the chord distribution. The PIA's results were poor and inconsistent to begin with, but semi-decent results were obtained after developing the methodology. The total counts registered by the PIA in a single trial proved to be an indicator of the results. Good results came from total counts above 1 000 000. The PIA's video display was another useful tool for developing the experimental method. The methodology developed for the PIA worked by initially lowering the lignin concentration. Then the lignin was dosed or sampled in by turning off selected pumps which led to consistent results. Further improvements are still needed if the PIA is to be used in laboratory or industrial settings.

Keywords: Lignin, precipitation, FBRM, PIA, chord

Contents

Background

Biorefinery/introduction

Modern society is built on a foundation of cheap and plentiful fossil fuels. These fuels are a finite resource and are becoming increasingly more expensive to extract (Roeger 2005). As easily available deposits run out, harder challenges must be met by more expensive technology to continue extraction. The cost of fossil fuels has increased but there is also an environmental perspective to consider. Global warming with its resulting climate change is a concern. The price of crop failure and climate change migrations (Leatherman 2001) are currently disconnected from the actual price of oil. The cost from such issues will need to be addressed eventually and can as such be seen as an associated cost to the fossil fuels.

Finding alternatives to fossil fuels is thus of interest. They are however difficult to replace due to their suitability as fuels and chemical feedstock. Fossil fuels sheer convenience in industrial processing is also a factor. Progress has and is being made, however. Some examples such as bio-based plastics, fibers and fuels made from straw, wood, vegetable oil and sugar plants have all been made with various degrees of efficiency (Aresta, Dibenedetto et al. 2015, Olsson, Sjöholm et al. 2017). Even if a complete replacement isn't possible, partially replacing fossil fuels with bio-based alternatives are a good way to lessen the impact on the climate. An example is the E95 petrol fuel in Europe where 5 % of the petrol is replace with ethanol.

As the world's population grows, land usage increases in intensity and in area of land under cultivation. The raw material used in the biorefinery must thus come from food production leftovers or more marginal land unsuitable for farming. That means that wood, algae or straw/grasses (Aresta, Dibenedetto et al. 2015) are of interest as raw feedstock for chemicals and fuels. As the processes based on these materials develops and demonstrates possibilities of profitability, industries seeking any advantage over their competitors will find the new methods very intriguing. The paper industry for example are looking for new opportunities as the increased digitalization of the world leads to a shrinking newspaper consumption. Shifting the production into new areas would thus generate profits especially if the raw materials were previously considered waste. Older mills may even be able to increase production. In many plants the production bottle neck is the recovery boiler where the black liquor is burnt for production of electricity and process steam, but also recovery of cooking chemicals. If part of the biomass can be processed into a market commodity, capacity is freed up in the recovery boiler that can be used for increased production of the main process. Kraft lignin is a promising possibility in this regard as lignin is normally burnt in the furnace of Kraft pulp plants.

A bio refinery based on Kraft lignin offers many possibilities but also has challenges that need to be addressed. Kraft lignin is a very complex molecule with an irregular chemical composition, shape and size making it difficult to process. Kraft lignin is also distinctly different from the natural lignin in wood. A recent development is the Lignoboost ™ process which separates Kraft lignin from the black liquor in the Kraft mill. The Lignoboost ™ process consists

of several steps: a Lignin precipitation step, filtration, re-slurring of the filter cake, another filtration step and a final washing (Öhman, Wallmo et al. 2007). The process produces a lignin that has a lower ash content and a higher dry content than other alternatives (Wallmo, Theliander et al. 2009). Products such as carbon fibers (Meek, Penumadu et al. 2016), fuels and aromatics (Azadi, Inderwildi et al. 2013) are all possible products emerging from Kraft lignin and the Lignoboost ™ process.

An overview of how the Lignoboost ™ process would be used in an industrial setting goes like this: a part of the black liquor stream in the Kraft mill is diverted, has its pH lowered, causing the lignin to precipitate out of the solution. A filtering stage then forms a cake of lignin with a rather low purity. The cake is re-suspended in the previously used wash water with added acid. Finally, the slurry is washed again, this time with acidified washing water producing a cake with very high purity. This process avoids the problems with high filtering resistance in normal, older filtration and precipitation processes not using acidic washing liquid. As a result, the need for extremely large amounts of washing water or large filter areas are avoided (Tomani 2010).

To improve the process further greater understanding is needed regarding particle formation. Particle formation will be further discussed in the "Precipitation/particle agglomeration of Kraft lignin" section. The filter cake formation and filtration resistance are highly dependent on particles size and the size distribution(Tarleton and Wakeman 2005). Investigating these factors is thus important and have been performed previously (Sewring 2017) by using FBRM® (focused beam reflectance measurement). In this work FBRM® is used alongside a new method for determining the particle size distribution. The new method uses a particle size analyzer called PIA (particle image analyzer) built and owned by Valmet® based on optical measurement. The particle size distributions from both methods are compared to each other with the combined result used to deepen the understanding of the lignin precipitation process. An experimental procedure for using the PIA has been developed over the course of this work.

Particle size measurement methods

Measuring the precipitation process is of interest from a scientific and an industrial perspective. FBRM® can be used *in situ* both in a lab and in a mill. The allocation procedure of the FBRM® can be adjusted in order to assign more focus on the most likely particle size. For well mixed solutions with particles that respond well to the chosen laser wavelength it gives an accurate summary of the particle dimensions. The FBRM® has weaknesses however: It is unable to measure below one μm and measures the chords of particles, which may be difficult to convert to particle size in some cases. For a spherical particle, statistic ensure that the measure chord length will likely correspond rather well to the diameter. Non-spherical particles chord lengths can however be significantly different to its actual size.

The PIA is also intended to be used in a mill and its suitability for this along with possible strengths and weaknesses will be investigated. Particle size investigation can be done with light scattering methods such as the FBRM® as well as optical methods such as image analysis which the PIA uses. The PIA is of great interest as it has the possibility of measuring the shape of the lignin particles which the FBRM® is unable to do. The accuracy of the PIA is unknown

however and must be investigated. Another issue is the possibility of particles lining up behind each other as the camera in the PIA takes 2-D images. This possibility and its influence on the results might be too large for particle-dense solutions.

Sedimentation (Contado, Ravani et al. 2013) and sieving (Plana, Carpentier et al. 2018) are two other methods that can be used to determine particle size. Both can be done in several ways using various types of equipment. Sieving is best done with particles that do not stick to each other after they have formed as it risks forming a cake, capturing particles that would pass through the apertures. This method is obviously ex *situ* and works best on larger particles above 60 µm. Combing sieving with other measurement methods such as electron microscopes allows a glimpse of how the particles of different sizes look. Sedimentation requires that the density of the particles is known and cannot be done *in situ.* Very small particles in the micrometer range are difficult to measure with sedimentation.

Kraft lignin/Kraft process

Wood is a complex material composed of mostly cellulose, hemicellulose and lignin (Sjöström 1993). The structure of wood varies to a large extent on the type of tree species adding to the complexity of the material. The two main sub-groupings are softwood, such as pine, and hardwood, such as oak (Sjöström 1993). Cellulose remains the same among all species while the hemicellulose and lignin differs between species. Cellulose are chains of glucose units combined into a homopolysaccharide. The hemicelluloses come in many variants, but there are trends common to the two types of wood. In softwood the main types of hemicelluloses are (galacto)glucomannan and arabinoglucoronoxylan. In hardwood the main types are glucuronxylan and glucomannan.

Lignin is a very diverse and branched polymer constituted by phenylpropane units. There are three monolignols units guaiacyl, syringyl and p-hydroxyphenyl that can bond with the propane units, resulting in a very complex molecule with a diverse molecular structure. The most common monolignol unit in the lignin depends upon which type of wood it is. Polymerized guaiacyl units or coniferyl alcohol is the most common in softwood. Syringyl propane, sinapyl alchohol and guicacyl propane is more common in hardwood with guiacyl and sinapyl being the most common with different ratios depending upon the tree species (Higuchi 1997). Complex radical reactions catalyzed by enzymes combine these molecules, constructing the final lignin molecule. These units are connected to each other by covalent carbon-carbon or ether bonds of which approximately half of all bonds is the β-O-4 bond depending upon tree type. Soft and hardwood also have different ratios of the monomers to each other. The irregular manner of these bonds is what forms the branching and unsymmetrical structure of the larger lignin molecule (Sjöström 1993).

Adding to the complexity of the overall lignin molecule are the different functional groups present. Methoxyl, phenolic hydroxyl, aliphatic alcohol and carboxyl groups are all present in various amounts depending upon the wood species. There are other, rarer groups adding to the lignin molecules complexity. All these variations and option come together with a marked structural difference in the lignin depending upon where in the cell it comes from. Lignin is also bonded to the carbohydrates present in the cell *i.e.* hemicelluloses, named lignin carbohydrate complexes LCC's.(Sjöström 1993)

In the pulping process the structure of lignin changes greatly, from native lignin to what is referred to as technical lignin *e.g.* kraft lignin (Sjöström 1993), which is of interest in this work. The kraft lignin is formed as a result of the kraft pulping process. The Kraft pulping process is as follows (Sjöström 1993): Wood chips enter a impregnation chamber where the cooking chemicals impregnate the chips. Then the chips enter the digester and are heated up to the cooking temperature (150-170 °C) at elevated pressure. It is in the digester that the cooking reactions take place. Controlling the temperature, time and cooking chemicals present is of great importance to ensure a high yield of cellulose and hemicellulose. Lignin have been treated as an as a byproduct as the main purpose of the cooking have been to separate the primary product cellulosic fibers and hemicelluloses from the lignin.

The highly alkaline conditions in the digester causes the cooking chemicals, NaOH and Na_2S to react with the lignin. The produced kraft lignin will thus contain some of the sulfur from the Na_2S. As the main purpose of the cooking is to delignify the pulp, a great quantity of the β-O-4 bonds are cleaved resulting in an increase of the number phenolic hydroxyl groups. This obviously alters characteristics of the kraft lignin molecules from the native counterparts. There are other reactions occurring to varying degrees but the most common one is the breaking of the *β*-O-4 bond mentioned above. There are also reactions with lignin molecules containing *β*-aryl ether bonds that results in different compounds depending upon the present molecules in the local environment. Ether bonds can be cleaved by hydroxide ions, mostly resulting in formaldehyde. Lignin can be demethylated by hydrogen sulfide ions and have a variety of possible condensation reactions. These condensation reaction links phenolic groups together, slowing the delignification (Sjöström 1993).

After the kraft process the kraft lignin is still present inside the wood cell necessitating transportation out of it. Mass transportation occurs here by diffusion, with the smaller molecules emerging faster from the wood tissue(Sjöström 1993). The resulting liquor is then separated from the pulp in the washing stage resulting in black liquor. Various separation stages are used to remove pollutants and larger particles/solids before proceeding to the extraction of lignin from the black liquor, *e.g.* by means of the Lignoboost™ process. The concentrated liquor entering the recovery boiler has a dry content around 70 percent or higher. In general, some 40-50 % of the organic material in the black liquor is various forms of kraft lignin. About a third is various hydroxyl acids. Formic acid, acetic acid, extractives and other compounds makes up the rest of the organic matter. The remaining cooking chemicals are present as various inorganic ions. The general characteristics of kraft lignin follow certain trends but vary widely: More phenolic hydroxyl and carboxyl groups are present after the pulping process. The bonds between aromatic rings have also been changed (Sjöström 1993).

The process of acidification of a concentrated black liquor to precipitate lignin have been known for some time(Merewether 1961). Lignoboost™ is a far more effective process, rendering a higher yield with lower ash content and at a lower cost due to lower filter areas needed and less acidic washing required (Tomani 2010). The Lignoboost™ process then separates solid kraft lignin from the liquor through filtration. Consequently, since solid material has to be formed, the solubility of the kraft lignin is of vital importance(Zhu, Westman et al. 2014). The overall kraft lignin is a molecule with a negatively charged surface at a high

pH: this is due to the ionizable groups being ionized at sufficiently high pH. The temperature at precipitation also have an effect, as lignin precipitation yield increases as the temperature decreases. Around 85 °C precipitated lignin also becomes "soft" and "tacky" (Uloth 1989). Moreover, the size or molecular weight of the lignin macromolecules influences the solubility (Zhu, Westman et al. 2014).

Precipitation/ particle agglomeration of kraft lignin

Experiments indicate that phenolic groups and ionization of said groups are a critical factor for the solubility of kraft lignin in aqueous solutions (Sewring 2017). Increased ion strength increases the yield of precipitated lignin and so does a lower pH. The temperature also has an effect, *e.g.* it affects the activity of the hydrogen ions. Other temperature effects may be possible but is not certain as literature indicate. Lower pH increases the amount of small lignin molecules precipitated which may be due to those having a larger ratio of phenolic hydroxyl groups (Zhu, Westman et al. 2014).

A kraft lignin macromolecule has a very complex and unregular structure but some particular properties are suggested to be important for precipitation(Sjöström 1993). The molecule has many ionized groups that orient themselves outwards, preventing the separate molecules from agglomerating and precipitating out of the solutions. To precipitate the lignin, the solubility is decrease by protonation of phenolic groups as negatively charged phenolic groups play a critical role for the repulsive forces between lignin macromolecules and particles. With enough H^+ ions in the aqueous phase the phenolic groups are protonated forming a new near neutral surface layer. When the surface has been sufficiently protonated the van der Waals and other hydrophobic forces dominate the overall interaction. The molecules then aggregate, forming solid particles which may grow in size and/or agglomerate further, i.e. precipitating out of the solution(Sewring 2017).

Experimental

Method/experiments

The experimental procedure was as follows: first solid lignin blocks were ground to powder and dissolved in a mixture of distillated water and sodium hydroxide. The sodium concentration was set to 0,8 molal with the lignin making up 18 percent of the total weight. The concentrations of sodium and lignin were diluted to half of the above-mentioned values by using distilled water. The solution was then filtered using regenerated cellulose filter paper. After that the solution is precipitated using sodium chloride (6 M) and hydrochloric acid or sodium sulfate and sulphuric acid (6 M). During the precipitation the FBRM® was used to monitor the formed particles. The final step was to analyze the obtained lignin suspension from the precipitation-stage using the PIA (particle image analyzer). The PIA needs to dilute the suspension in order to be able to distinguish individual particle. The dilution liquid used was a mix of distillated water and sodium chloride or disodium sulfate, corresponding to the salt used in the precipitation. The pH of the dilution liquid was matched to the pH of the suspension of precipitated lignin using sodium hydroxide and the same acid as in the precipitation. A scheme of the process is shown in Figure 1.
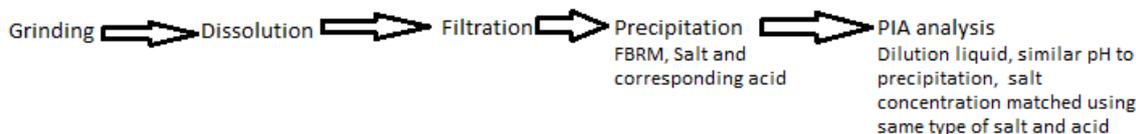

Figure 1:Flow scheme of how the experiments were performed

The experimental procedure conducted in this work is similar to an earlier study (Sewring 2017). The lignin used in all experiments is a softwood kraft lignin produced at a Nordic pulp mill extracted by the Lignoboost™ process. The lignin used in these experiments comes from the same batch that was characterized in (Aminzadeh, Lauberts et al. 2018): The ionisable groups on the lignin, phenolic and carboxylic groups were found in contents of 4,27 mmol/g and 0,45 mmol/g respectively. The aqueous solution for the experiments were made by ball-milling lignin and mixing it with deionized water and NaOH (Sigma Aldrich, purity ≥ 98%). The salt used in the aqueous solution to achieve precipitation and increase salt concentration level was NaCl (Sigma Aldrich, purity ≥99,5%) and Na_2SO_4 (Fisher Chemical, purity ≥99,5%). The same salt used in the dilution liquid was NaCl (VWR chemicals, assay 100%) and Na_2SO_4 (VWR chemicals, assay ≥98%) mixed with deionized water. The acid used for acidification was a 6-molar solution of HCL (VWR chemicals, 37%) and H2SO4 (Emsure, 95-97%). The pH adjustments to the dilution liquid was done by addition of NaOH (Sigma Aldrich, purity ≥ 98%) tablets and respective acid for the experiment.

Experimental overview

Table 1 gives an overview of all performed experiments. In all cases measuring the pH was done by removing part of the solution and cooling to room temperature before measuring.

The sample was then returned to the vessel. The temperature of the samples for the pH-measurements varied with the lowest at 20°C and highest at 27°C. In general, the lignin suspension used in the PIA would be at room temperature, somewhere between 23 and 25 degrees Celsius. The temperature of the dilution liquid was 20-22 degrees °C. The salt concentration in table 1 is the final concentration in the aqueous phase of the lignin suspension. The salt concentration was 3 molal in the dilution liquid for all experiments except the one where the lignin suspension reached a 4 molal concentration in which the dilution liquid concentration was also prepared correspondingly.

Some experiments were conducted to reach the onset of formation of micron-sized particles while others proceeded beyond that. Experiment 4 was carried out without heating. Experiment 26 was carried out to see if lowering the temperature after onset had occurred had any effect. The experiment reached onset, was salted until final concentration was reached and was then left under agitation in the precipitation vessel overnight. The lignin concentration in the experiments started at 10 % to compare with previous studies (Sewring 2017). As insight was gained into the operation of the PIA over the course of this study a decision was made to start lowering the lignin concentration. The concentration was halved after experiment 12 and then halved again after experiment 13. As a better experimental method for the PIA was developed and proper results were obtained the lignin concentration was raised to 5 and 10 percent again.

Preparation

Lignin is dissolved in an aqueous solution of 1 M NaOH and mixed at least over night before being filtrated at room temperature. Experiments 1 through 18 were filtrated with a regenerated cellulose filter of type 184 Sartorius stedim, with a pore size of 0,045 µm. The later experiments used filters from Munktell, quality 5, diameter 100 mm. The filtration was performed by using a Buchner funnel inserted into the neck of a glass flask by vacuum suction. The rate of material caught by the filter varied as the success of every filtration was not uniform. The most common error occurred when the filter paper did not seal uniformly but left a small flap which allowed the solution to bypass much of the filter. The lignin content was 10, 5 and 2,5 % in different experiments but all the solution had a molar content of NaOH of 1 Molar.

Table 1:Table of all planned experiments

ID	Temp.°C	Salt type	Na concentration molal	pH fin	pH Dilution	Lignin %	Note	Counts
1	65	NaCl	3	10, 7	NaN	10	FRBM ® only	
2	65	NaCl	Onset	10,4	10,4	10		
3	65	NaCl	Onset	10,4	NaN	10	FBRM ® only	
4	25	Na_2So_4	3	9,6	NaN	10		
5	65	Na_2So_4	3	10,3	≈10	10		
6	65	Na_2So_4	3	10,6	11	10		
7	45	Na_2So_4	3	10,3	11	10		
8	45	NaCl	3	10,4	≈10	10		
9	55	NaCl	3	10,6	≈10	10		
10	55	NaCl	3	10,2	10,1	10		
11	55	NaCl	3	10,5	10,3	10		
12	55	NaCl	3	10,9	11,1	10		
13	55	NaCl	Onset	10,	≈10	5		
14	55	NaCl	Onset	9,7	9,6	2,5		
15	55	NaCl	2,5	9,3	9,1	2,5		
16	55	NaCl	2,5	10	9,9	2,5		
17	55	NaCl	4	9,8	10,4	2,5		
18	55	Na_2So_4	3	8,9	8,9	2,5		
19	55	NaCl	3	10,3	10,4	2,5	New filters	
20	55	NaCl	3	10	10,3	2,5	Started dosing	
21	55	NaCl	3	9,4	9,6	2,5		
22	55	NaCl/	3	10,3	10,2	2,5		
23	55	NaCl	3	9,4	9,3	2,5		
24	55	NaCl	3	8,8	8,9	5		
25	55	NaCl	4	10,3	10,5	10		
26	55/25	NaCl	3	9,7	NaN	10	Heat trial	

The precipitation vessel was a 0,5 L jacketed glass vessel with an inner diameter of 96 mm. A metallic (stainless steel) baffle was inserted to control the mixing pattern. The mixing was done by a pitched-blade impeller approximately situated 15 mm over the vessel's bottom. The impeller diameter was 50 mm. The agitation speed was set to 250 rpm, providing good mixing. The heat needed to reach the experimental temperature was provided by indirect heating via the jacket. The FBRM® probe itself was placed at an approximately 35-degree angle towards the flow, ensuring that enough particles passed close to the window at the tip of the probe.

This placement of the probe prevents lignin clogging of the window and thus poor measurement.

Most of the FBRM® experiment were designed to salt out the lignin. The other experiments had the salt added beforehand and was then acidified with acid until precipitation. Salting out a solution works by increasing the concentration of the counter ions until they cause the lignin particles to agglomerate. This was done by lowering the pH of the solution to approximately 10 and then salting until onset occurs. Onset occurs when the total amount of chords increases rapidly and stable particles larger than 1 µm are recorded.

Some of the experiments have more salt added after the initial precipitation occurs to investigate if and how the solution/particles changes upon further increase in salt concentration. At the end the pH value was measured, and the dilution liquid was adjusted to the approximately same value. This is done with NaOH tablets and the same acid used in the lignin solution precipitation.

After the precipitation had occurred and the FBRM® measurements were finished it was the PIA's turn. A small part of the liquid was poured into a vessel with a mixing provided by a magnet stirrer. Two pipes corresponding to a in and outlet of the internal mixing chamber of the PIA was placed in this vessel. The lignin solution was then pumped to the mixing chamber where it meets the dilution liquid. The resulting mixture is pumped to a camera lens which records footage that a computer algorithm analyzes, counting particle size and volume among other things.

FBRM®

Focused beam reflectance measurement is based on the scattering of a laser as its focal point crosses the path of particles. This can be done *in situ,* as in the performed experiments, or *ex situ*. The machine utilizes the phenomena of back scattering and interference of light of the beam emitted by the machine. The beam is focused at the glass window of the probe. The beam is then rotated, scanning the suspension in a circular pattern at a high speed (2 m/s). By using the time of the pulse of the backscattering and the speed of the circular motion of the beam the chord length is determined. Measurements are reported in the 1-1000 µm range. The measured particle is then recorded as a count and assigned to a specific channel corresponding to a given chord length interval. The channels are unevenly spaced with half of the channels designating chord length shorter than 30 µm. The specific model used in this case was a G400 from Mettler Toledo.

PIA

The equipment noted as PIA is a particle size analyzer using an optical method. The method has been used *ex situ* in this case as the liquid to be analyzed is fed to the machine after precipitation has conducted in the precipitation vessel monitored by the FBRM® *in situ*. When comparing the two methods it is the final sampling point from the FBRM® that is compared to the results from the PIA. After some experiments it was determined that it is beneficial to

keep the lignin suspension under agitation during any duration of time between the precipitation-stage and the PIA-procedure in order to prevent sedimentation.

The machine itself is a combination of different devices. The camera is a Valmet® automation microscope with a 0,5 mm cuvette. A Valmet® PC operates the camera and the computer program it uses to count and determine the size of the particles in the solution. There are four pumps which distribute the two liquid streams. There is the dilution pump, an IWAKI EWN-B31VC-ER feeding dilution liquid into the system. The dilution liquid is designed to have a sodium ion concentration as close as possible to that of the lignin solution. In the onset experiments the lignin solution was precipitated but no more salt added after that. The dilution solution however had a salt concentration of 3 Molar. The pH is adjusted using NaOH tablets and the same acid as used in the FBRM® i.e. HCl or H_2SO_4. The dilution tank can heat the dilution liquid up to 30 degrees. The heating elements was not used as 30 degrees is far below the temperature in the precipitation stage. In addition to the temperature difference the heating element was small and would take a long time to heat the tank to desired temperature.

The camera pump is a Grundfoss Alldos DDA 17-7-FCM PV/T/C-F-31U2U2FG pump and supply the mixed liquid from the mixing vessel. The mixing vessel mixes dilution liquid from dilution tank and sample liquid pumped in by the sample pump, a Watson Marlow 323S/D Perisferal pump. The sample pump pumps liquid from an internal circuit that that is pumped around by the circulation pump. The circulation pump Watson Marlow 530S Perisferal pumps is thus the one which pumps in the sample liquid in the first place. As this is a new type of device under development the experimental method was slowly developed over the course of the study. The camera works by initially taking a background image. The image is then referred to as a reference for incoming measurements. It is thus of utmost importance that the image is clear from impurities. The camera then films the liquid and a computer algorithm compares the recorded images with the saved background image. The program then begins processing the video/pictures during a set time interval. A total length is decided which is then divided up into active segments where the computer calculates and inactive ones where it does not. Multiple such time intervals can be processed during an experiment, each yielding a set number of results.

The problem that have been present in these experiments is likely one of oversaturation. The background image has been completely covered with particles making it impossible for the camera to distinguish separate particles. The computer also only counts particles from 0,1 to 103 micrometers. If several smaller particles, then line up in such a way that the camera confuses the mass for a single particle larger than 103 micrometers that mass will not be counted at all. This line up and disregard of particles above a certain size is likely what is responsible for the failed trials at a 10 % lignin. The trials that were successful came from the trials where the camera cuvette was in the process of emptying or filling thus having a lower concentration. The camera was at these moments able to distinguish separate particles.

The trial results were very uneven and not something that could be accurately said to represent the particles in the solution. To avoid this, the concentration in the solution was dropped to first 5 % and then 2,5 % lignin. The 5 % had the same problem with the results but

was deemed to be a step in the right direction. The 2,5-percentage produced even and visible results during the experiments. The results were not at all close to the FBRM's results.

The volume distribution had seemingly formed a mostly even ridge over all measured particles instead of a similar curve as seen in the FBRM® results. When compared to the results from the FBRM® it was clear that something more was needed. Trying to vary the pumping speed did not appear to produce any visible changes. Eventually a method was found. The circulation pump allowed to introduce some lignin solution and then turned off. This diluted the solution entering the camera house enough to produce even and repeatable results. The volume distribution formed a curve and reported much larger number of particles than what had been previously had. This was initially done with 2,5 % percent. Increasing the lignin concentration to 5% yielded even larger counts and repeatable results. Finally, the same method was tried with 10 % to no success.

Data treatment/Assumptions

The data shown in the Results section is an overview of the full list of experiments. The FBRM® data is as mentioned earlier divided into various channels corresponding to specific chord lengths. The channels have a minimum length and a midpoint length. A particle chord count percentage was plotted by summing up the count, dividing individual channel counts by the total count and multiplying the results with 100 %. The particles are assumed to be perfectly spherical. A spherical particle is more likely to be placed in the somewhat correct channel, with respect to the particle size, as most possible straight lines over it will be close to its diameter. If the particles are unevenly shaped it becomes much harder to interpret the FBRM® measurements as the measured chords will not line up very well with the actual particles. For perfectly spherical particles the drawn chords on the particles will be assigned to the correct channels due to statistics and the particles shape. This is due that if one considers a sphere as a flat circle and drawn a straight line over it most of those lines lie close to the center and thus the diameter of the circle.

To compare with PIA the volume percentage was also plotted. The midpoint chord length was assumed to be the diameter of the particles. As in previous assumptions the particles are assumed to be perfectly spherical. The volume percentage distribution is more sensitive to deviations from perfect spherical particles as the measured unit is raised to the power of three. The volume for a single particle in every channel is thus determined. The volume distribution as a percentage is calculated by multiplying the spherical volume of a single particle with the number of chord counts, adding the volumes together. With the total volume calculated the total volume for each specific channel is divided by the total volume measured and then multiplied with a 100 %. Since the midpoint length is raised to a power of three this causes even small count of larger particles to shift the volume distribution to larger particles. As the chords become larger the accuracy becomes smaller with 50 unevenly spaced channels between 30-1000 micrometers. Low, often almost singular counts for larger chords easily distorts the distribution. Some caution must thus be taken when considering the results.

The PIA gives a list of data concerning various properties of the particle solution. The data used is the volume distribution. This data is given in the form of a list of volume percentages. The data is divided up into 1 micrometer intervals from 0 to 103 micrometers. The volume percentages are then plotted in Matlab® in to ensure a constant x axis. These are the plots in the results.

Results/discussion

Experiment table

Table 2: Results table for performed experiments

ID	Temp.°C	Salt type	Na Conc. molal	pH fin	pH Dilution	Lignin %	Note	Counts FBRM®/PIA
1	65	NaCl	3	10,7	NaN	10	FRBM® only	33000
2	65	NaCl	2,6	10,4	10,4	10	Onset	69000/1150000
3	65	NaCl			10,4	NaN	10	Data lost	33000
4	25	Na$_2$So$_4$	1,4	9,6	NaN	10	Gelation	15
5	65	Na$_2$So$_4$	3,1	10,3	≈10	10		19000/1659000
6	65	Na$_2$So$_4$	3	10,6	10,9	10	Heat tube broke	101000/NaN
7	45	Na$_2$So$_4$	3	10,3	10,9	10		69000/112000
8	45	NaCl	3	10,4	≈10	10		88000/540000
9	55	NaCl	3	10,6	≈10	10		71000/2300000
10	55	NaCl	3	10,2	10,1	10		91000/940000
11	55	NaCl	3	10,5	10,30	10		61000/1500000
12	55	NaCl	3,5	10,9	11,1	10	Acid miss	71000/105000
13	55	NaCl	2,0	10	≈10	5	Onset	90000/1300000
14	55	NaCl	1,6	9,7	9,6	2,5	Onset	69000/1300000
15	55	NaCl	2,5	9,3	9,1	2,5		93000/1100000
16	55	NaCl	2,5	10	9,9	2,5		67000/840000
17	55	NaCl	4	9,8	10,4	2,5		83000/630000
18	55	Na$_2$So$_4$	3	8,9	8,9	2,5		89000/780000
19	55	NaCl	3	10,3	10,4	2,5	New filters	20000/81000
20	55	NaCl	3	10	10,3	2,5	Started dosing	13000/1400000
21	55	NaCl	3	9,4	9,6	2,5		68000/1400000
22	55	NaCl	3	10,3	10,2	2,5		57000/1500000
23	55	NaCl	3	9,4	9,3	2,5	Only sample pump	85000/2600000
24	55	NaCl	3	8,8	8,9	5		86000/3200000
25	55	NaCl	4	10,3	10,5	10		57000/0
26	55/25	NaCl	3	9,7	NaN	10	Heat trial	110000/NaN

Table 2 shows how the experiments were performed and there were some changes to what was planned. The third experiment was performed but the raw data was lost. Experiment 4 was done to see how precipitation occurred at room temperature: it was found that the lignin formed a gel. The liquid was too viscous to be examined with the PIA and the gelation occurred before onset. The data from the FBRM® was not very reliable with the chord distribution very different from all other results. As the FBRM® relies on a flow high enough to move the

particles past the probe window the results from the viscous solution is not trustworthy. The gelation was also likely built up of a network of particles smaller than 1 µm.

From experiment 5 to 20 various pumping ratios were tried in order to improve the results from the PIA, but no obvious improvements were obtained from those changes. The real changes instead came from the variation of the lignin concentration. As of experiment 20 a new method of running the PIA was tried. The method worked by dosing in the sample liquid into the mixing chamber. The circulation and sample pump ran for a short time and then was then turned off. Further improvements came during experiment 23 when only the circulation pump was turned off. With a working method the concentration was restored to five percent and then ten percent. The lignin concentration of five percent produced reliable results, but the 10 percent solution produced blanks only.

In the final experiment the lignin was precipitated at 55 °C. After waiting a few hours to allow the chord distribution to reach a steady state the heating was turned off. This was done to see if and how the lignin solution would change.

FBRM®

Course of precipitation

In general, the course of precipitation occurred in two forms. An initial rapid growth followed by stabilization with a slight decline in some cases. The other form was a slower growth that was more constant and tapered off at steady state. The growth in **Error! Reference source not found.** is of the second type. The growth that happened in experiment 11 as shown in **Error! Reference source not found.** is of the first type. No clear correlation to pH, salt concentration or temperature was found. Instead the likely reason for the different forms is how far beyond onset the solution is when precipitation occurs. How much more salt or acid is introduced at once into the solution beyond what is needed for onset. The closer to the actual precipitation point the slower the growth is. A solution condition that has jumped beyond the onset point instead of closing in on it is likely to have the type of rapid growth that is seen in **Error! Reference source not found.**. The addition of salt after onset had occurred gave an initial jump in recorded chords that stabilized but did not shift the distribution. At the investigated conditions onset in general seemed to occur around 1,5 molal of sodium ions and around a pH of 10 and a temperature higher than 25°C. The actual system conditions at onset point was not determined.

In order to investigate the effect of temperatures on the precipitation experiment 14 was salted until it reached a point close to pervious onset points at room temperature. Then the heat bath was turned on. After an initial delay onset occurred. The initial growth proceeded without any variation but when the temperature reached a tipping point the precipitation accelerated before stabilizing at steady state. This is seen in Figure 2. While the actual temperature profile of the solution over time was unknown the initial temperature was 23 °C and the final temperature was 55 °C. There may be an onset temperature but there also appears to be a temperature where the kinetics of the precipitation increases. The result indicates that influence of the temperature, pH and salt concentration on the precipitation is in agreement with what is generally found in literature.
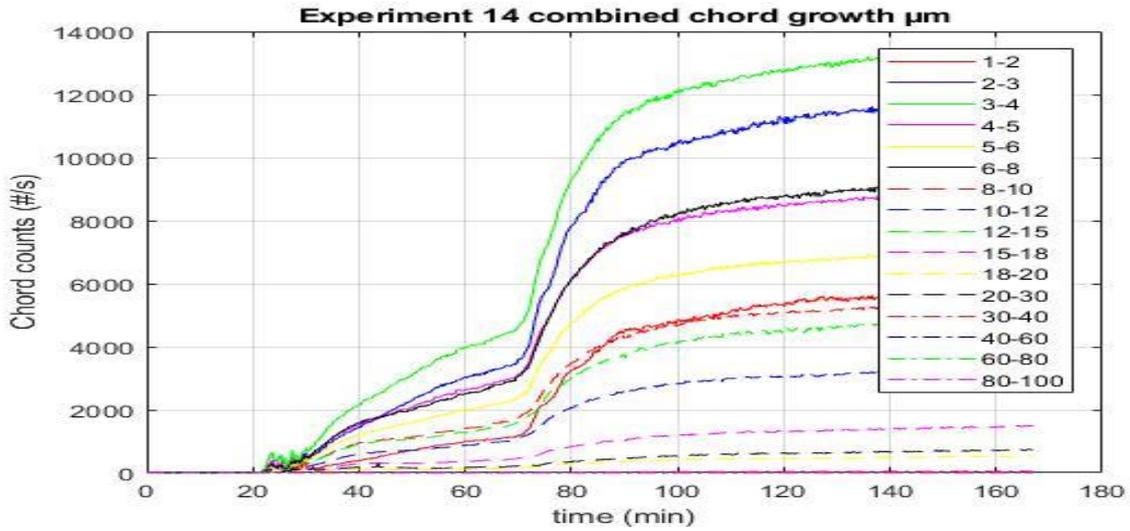
Figure 2: The chord growth over time for experiment 14 as seen by the FBRM, the temperature for the tipping point around 70 min is unknown
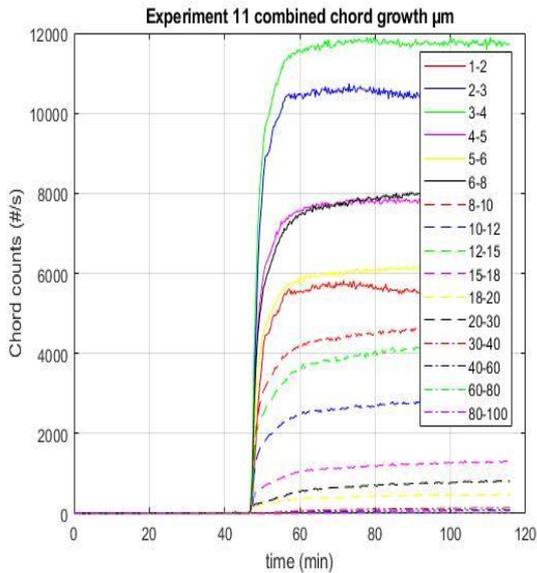

Figure 3: The chord growth over time for experiment 11 as seen by the FBRM
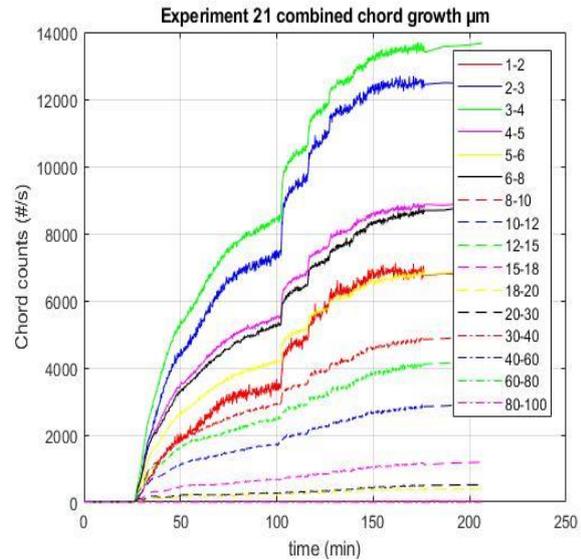

Figure 4: The chord growth over time for experiment 21 as seen by the FBRM

The final experiment checked if a lower temperature had any effect after precipitation had occurred. It was a salting out experiment that started at 55 °C with a pH of 10,2 measured at a temperature of 22,2 °C. Salt was added until the sodium concentration reached 3 molal. The solution was then allowed to settle, reaching a point where no new particles was detected. Finally, the heating element was turned off with the FBRM® left to run over night, cooling from 55 °C to room temperature. The final chord distribution was alike the distributions obtained from previous experiments. This indicates that the precipitated particles are stable with respect to time and at lowered temperatures. Some buildup of lignin gel in the precipitation vessel could be observed around baffles and other areas where the mixing was poor while the solution itself was virtually free from gelation. This had happened earlier for 10 % solution but

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not to this extent, the experiment that underwent gelation being the exception. Some buildup of gelatinous material happened during all the previous experiments with lower lignin concentrations producing smaller amounts of gelation. The larger build up was thus likely due to the experiments longer timespan. Lignin sedimentation and stickiness likely causes it to attach to areas where the turbulence is not as strong and then start growing over time.
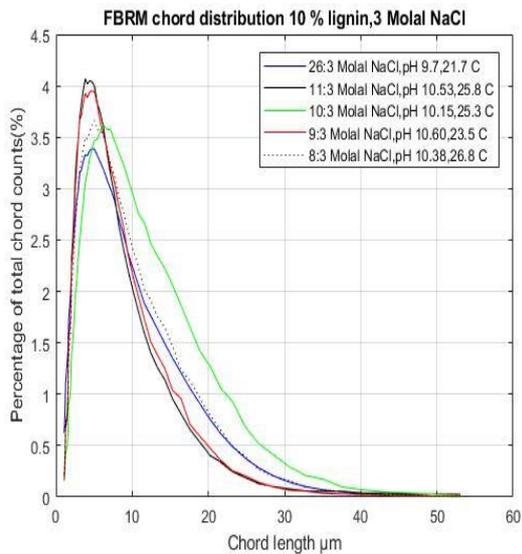
Chord distribution

Figure 5: The final FBRM chord distribution for various 3 molal NaCl experiments. The experiment numbers are the first numbers in the legend box

Figure 6: The final FBRM chord distributions for various experiment. The experiment numbers are the first numbers in the legend box

Figure 7: The final FBRM chord distributions for various experiment. The experiment numbers are the first numbers in the legend box

The chord distribution of the various experiments was virtually similar except for experiment 4 which gelation occurred. The distribution varied to a minor degree although not enough to indicate a significant difference due to any specified factor. As seen in **Error! Reference source not found.** and **Error! Reference source not found.** most of the measured chord lengths are in the 3-6 µm range. Slight changes of the chord length distribution exist between experiments but there were no divergences large enough to draw any conclusions from. The experimental factor that varied the widest was the amount of salt, 1,4-4 molal, and type, but they seemed to have had a minor effect on the distribution. The addition of more salt merely increased the number of recorded chords but did not change the distribution. The two salt types have no apparent effect when compared to each other as in Figure 7 and between that figure and **Error! Reference source not found.**.
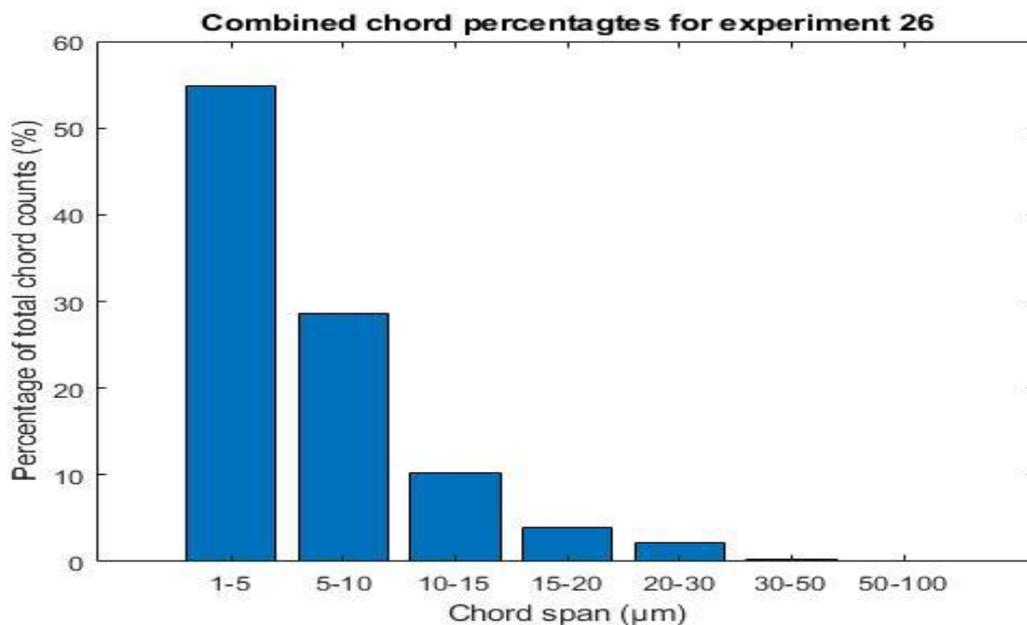

Figure 8: Experiment 26 has its different chord spans summed up into combined chord percentages

The FBRM® detects particles larger than 1 µm and thus of particles smaller than that cannot be analyzed. When combining the chord count percentages into spans and presenting them as in Figure 8 the particles smaller than 1 µm are not visually present. This could lead to an unreasonable conclusion that no particles smaller than 1 µm exists. There is instead likely a significant number of particles smaller than 1 µm. If it is assumed that the distribution follows a pattern somewhat like a bell curve it may be possible that the micron-sized particles account number-wise for most particles in the solution, however it remains unclear. The peak of the distributions bell curve may be in the 1-5 µm span but could very well be below the 1 µm limit of the FBRM®. These smaller particles are what likely formed the possible nanostructure responsible for the gelation that occurred in experiment 4.

PIA methodology

In the beginning of this study the PIA was a new piece of equipment that had been tested only in the sense that the different parts worked. Developing a method of using the device in a way that would produce good results was a large part of this study. To do this the PIAs volume distribution was compared to a calculated volume distribution from FBRM® data.
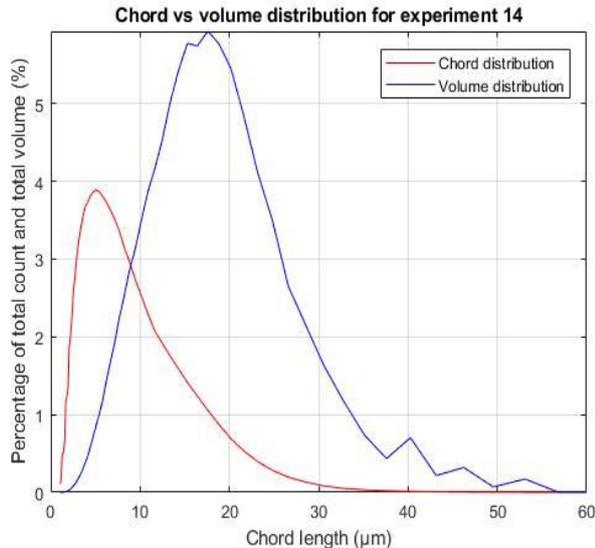

Figure 9: Experiment 14s chord distribution compared to its calculated volume distribution based on FBRM data
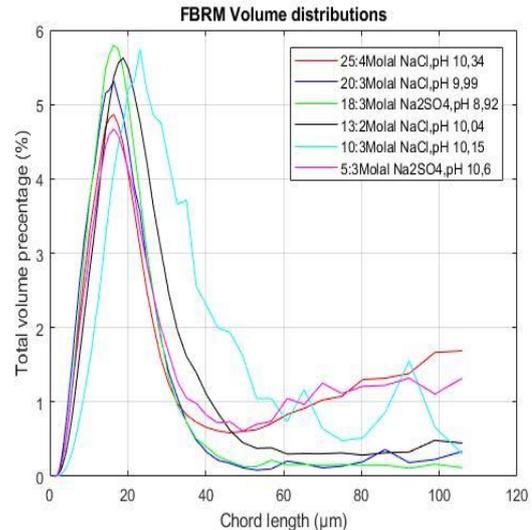

Figure 10: The same experiments shown in fig.6 displays its calculated volume distributions in above figure

Transforming the FBRM®'s chord distribution to a volume one, shifts the distribution as seen in **Error! Reference source not found.**. The figure shows that the volume distribution resides over a larger span and is focused differently with most of the volume being between 10-30 μm with the peak contribution coming from particles/chords around 18 μm. While the chord distribution was stable the volume distribution was less so. With the measured distance being raised to the power of three, smaller fluctuations that would have gone undetected in the chord distribution becomes much larger in the volume distribution. Still the volume distribution for almost all experiments forms curves like the one in **Error! Reference source not found.**. The general shape can be seen in **Error! Reference source not found.** for other experiments. The divergent lines are obvious but even they tend to peak around 18 μm.

The PIAs data was delivered directly from the computer in the device and the mathematics for its calculations are unknown but are probably comparable to the ones done for the FBRM® in some respects. A line is drawn over a particle captured in two dimensions by the camera which is then processed through an equation. Combing this for all particles the camera detects gives the volume distribution. These equations and algorithm were however unknown so are the effects they have on the result. An obvious problem here is the two-dimensional nature of the images. This risk distorting the images as particles can line up partially behind each other. If a line can be drawn, then in such a way that it passes from one

particle to another the computer risks counting several smaller particles as fewer large particles.

The early experiments had a lignin concentration of 10 percent and most of the results from these experiments were blank. The computer was unable to distinguish individual particles in the solution and thus reported the solution to be empty of particles. The trials that produced results reported very uneven distributions in the same experiments and between different experiments regardless of the experimental factors. The results came from the parts of the experiments when the camera house was being filled or emptied of the lignin solution. The video from the camera also showed a roiling black mass instead of a particle solution with the background visible. Changing the various pump ratios had negligible effect.

To resolve the issue of particle overload which rendering the camera unable to distinguish separate particle the lignin concentration was lowered. Initially the concentration was brought down to half, 5 percent but it was not enough to produce any real change. Most of the results were blank and only the results coming from when the camera house was being filled or emptied reported anything. Those results were uneven and unstable as well. Thus, the concentration was halved again to 2,5 % which started producing consistent results. With a concentration of 2,5 % no results were blank anymore and there were general similarities between different experiments. The results themselves were a bit disappointing however as they all followed a very general ridge shape as seen with the blue line in Figure . When compared to the FBRM® results they are vastly different. The results from the time when the camera house was being filled or emptied was also different looking more like the FBRM® results and reporting higher particle counts than what was ascribed to the ridge like results.
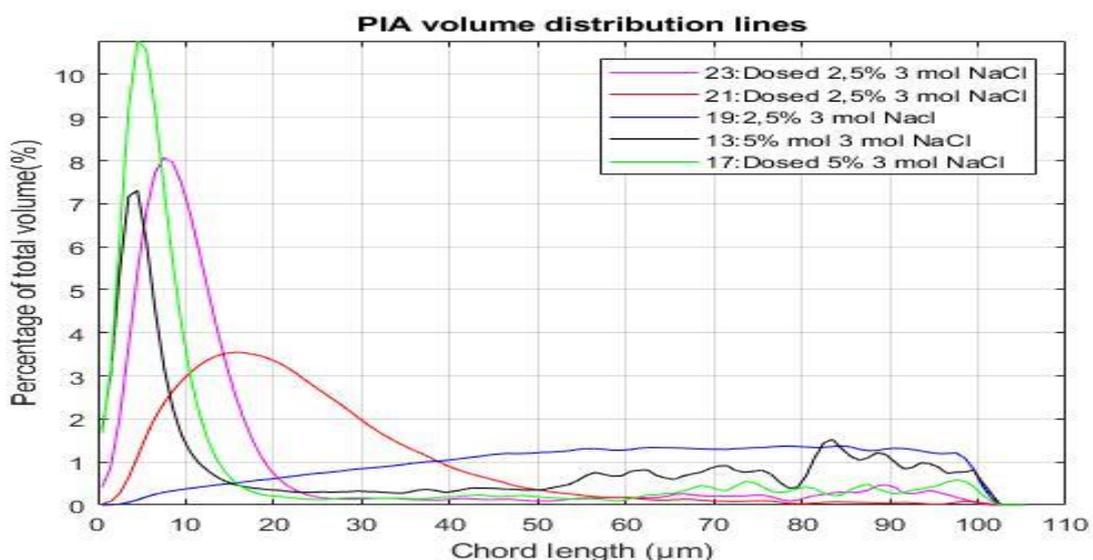

Figure 11: Chosen PIA distributions from various experiments with experiment number in the legend box.

At this point the lignin concentration was 2,5 % which is significantly lower than what is the norm in the pulp industry. In general, the lignin percentage of the strong black liquor varies somewhere between 20-36 % depending upon tree species and how far the evaporation has gone (Ek 2009). As the PIA is intended to be used both in industries and laboratories diluting

the sample liquid too far should if possible be avoided. Taking a clue from how the results closes to the FBRM® came from when the camera house was being filled or emptied an attempt was made to only introduce a little of the solution. This small sample was then recycled through the machine instead of continuously introducing new material and overwhelming the camera. Essentially a small part of the lignin solution was "dosed" into the internal circuit of the PIA. This was done by letting the dilution and camera pump run the entire time but only letting the circulation and sample pump run for a short time before being turned off. This dilutes the solution in the camera house much more and stops new lignin from overwhelming the sample in place. With this procedure the results improved markedly as can be seen in Figure . Shutting of the circulation pump but letting the sample pump keep running improved the end results even more which can be seen when one compares the purple line to the red line in Figure with the purple line being more focused and closer to the chord length distribution. With a working method the concentration was raised up to 5 % and gave satisfactory results. In the last PIA experiment the concentration as brought back to the initial value of 10 % but the solution proved too particle dense even with the method of only introducing a small sample.

Even with a working method of 5 percent a few questions remain. If one is to trust Figure part of the volume is always made up of larger particles with part of the volume being very evenly spread out over a particle length from 20-60 µm. After 60 µm and especially between 80-100 µm the contribution doesn't appear to fade but instead grows and does so unevenly. This could come from extremely few particles having significantly larger volume than a particle of smaller size would but could also be evidence of particle line up with the low contribution coming from the rarity of the events. There is also a sharp drop of around 103 µm after which no particles appear at all. The drop off is most visible for the blue line in Figure but can be seen to some extent in the other lines as well. This is believed to be a result of the algorithm ignoring counts beyond a certain size, likely to filter out contaminants or disturbance as the algorithm gives datapoints beyond 103 µm but reports them as empty.

FBRM® vs PIA

The initial experiments are not considered here as it was not until the "dosing" method was developed that good results were obtained. Thus, all the results here are from the "dosing" method and of lignin concentration being 2,5 and 5 %. The previous experiments were either unstable or blank. Eventually stable and consistent results were obtained but all of them looked like ridges with the total volume being evenly distributed over the possible particle lengths and not an expected curve.
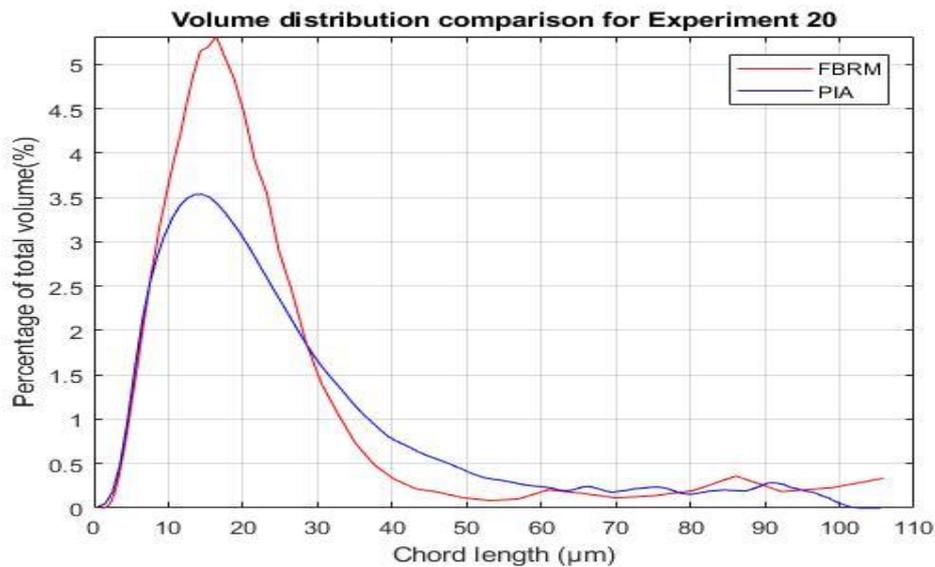

Figure 12: Comparison between the results from the FBRM® and PIA volume distributions for experiment 20

Experiment 20 was a salting out experiment with the temperature turned on after enough salt had been added to reach onset. The onset concentration was 1,9 molal. When the heat bath was switched on the solution eventually reached a temperature where precipitation happened. This initial growth in particles then reached a second point which led to an increased growth rate. Figure demonstrates the volume distribution of the FBRM® and the PIA with experiment 20 being the first experiment using the dosing method. As seen in Figure there is some overlay between the PIA and the FBRM®. The initial volume distribution is very similar with the first real differences showing itself for particles larger than 10 μm. The peaks of both the FBRM® and the PIA are close to each other on the x axis even if the PIA results are close to two percent units lower. Both also have some distortions coming from particles larger than 60 μm. The real difference comes from particles between 30 and 60 μm. The FBRM® s volume distribution rises quickly from 1 to 18 μm and then falls close to zero at 40 μm with the rest being distortions from singular particle counts. The PIAs volume distribution on the other hand decreases much slower with more of the volume coming from particles larger than 30 μm.

This discrepancy between the FBRM® and the PIA's results could come from larger particles that the PIA spots but managed to avoid detection by the FBRM®. Another possibility is that smaller particles line up behind each other and to the PIA then looks like a single large particle instead.
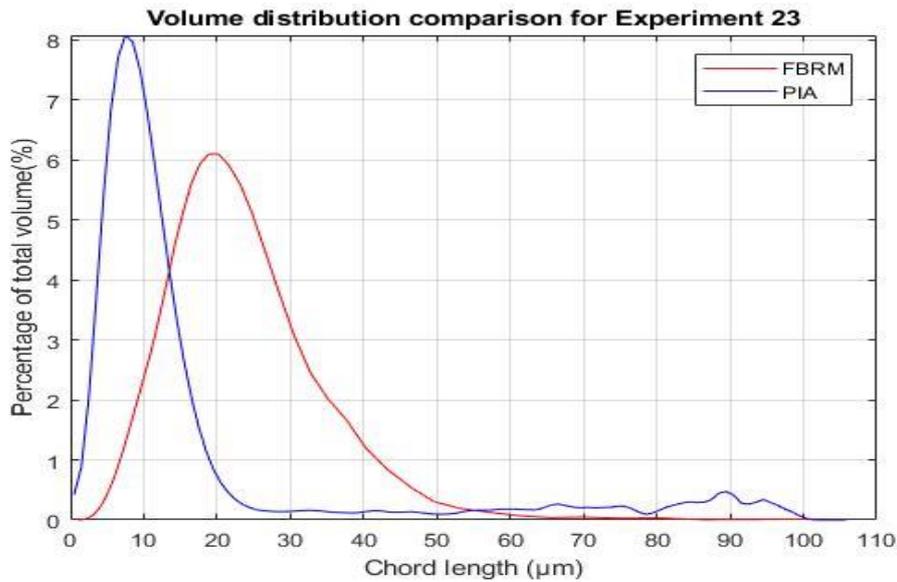
Figure 13: Comparison between the results from the FBRM® and PIA volume distributions for experiment 23

Experiment 23 was a salting out experiment with onset occurring after the total sodium concentration reached 1,8 molal. In the previous "dosing" experiment both the sampling and the circulation pump was turned off. In experiment 23 the sample pump was left on. This allowed the solution to be diluted even further shifting the volume distribution as shown in Figure . The PIA-distribution shifted to the left giving more weight to smaller particles than what is visible in the previous PIA results. The PIA is also clearly shifting away from the FBRM®'s results. The PIAs peak around 8 μm is almost 10 μm lower than the peak for the FBRM®. The FBRM®s volume distribution is very smooth in Figure while the PIA has some small disturbance around 60-100 μm. Particle line up is still present to some extent with as particles of all size appear to be present instead of there being gaps in the distribution or a fade out. How much particle line up shifts the results is unknown. The computer algorithm and the equations governing it is also unknown. The possibility that arose from Figure 8 that most of the particles are below 1 μm in length is of importance here. It could be that the volume distribution for the PIA in Figure has shifted due to particle line up from these smaller particles making it difficult to trust the shown distribution. This possibility could have an effect,

but one must consider that even if a majority of the particles are smaller than 1 μm the majority of the volume could instead come from larger particles rendering the issue moot.
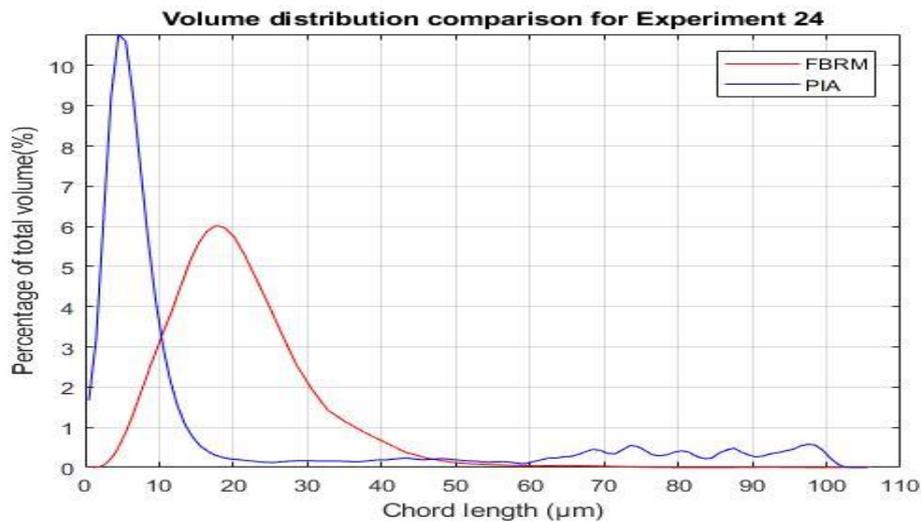

Figure 14: Comparison between the results from the FBRM® and PIA volume distributions for experiment 24

For experiment 24 it was decided to raise the lignin concentration now that the dosing method had proven itself. Thus, the lignin concentration for this experiment was 5 percent. Dosing was used with the circulation pump turned off. Onset occurred at a sodium concentration of 1,1 molal. Dosing produced consistent results while trying to run the PIA without dosing resulted in only blank recordings. The volume distribution for the PIA has shifted further towards smaller particles than the distribution in Figure but has also narrowed resulting in a much more focused distribution. The peak for the volume distribution is closer to the peak for the chord distribution but is far narrower having almost completely disappeared at the 20 μm while the chord distribution keeps going a little beyond that point. There is particle line up responsible for the disturbance from particles larger than 60 μm. Previously mentioned issues of particle line up combining with particles smaller than 1 μm is also likely to be present. In experiment 24 the dosing method was used for a 10 percent lignin solution but produced no results with the solution proving to dense at that concentration.

Discussion

FBRM®

The results from the FBRM® have been very consistent with each other despite the different experimental factors imposed. Salt type appears to have no effect on the chord distribution, or the precipitation process itself. The concentration of sodium between 1,4-4 molal in the solution appears to have very little effect on the actual size distribution with more salt simply increasing the amount of precipitated lignin. The precipitation process is somewhat sensitive to the amount of salt added but this sensitivity comes in the form of the growth rate after onset has occurred. The closer to the point of onset the slower the precipitation happens while an overshot result in an incredibly fast particle growth. How the amount of precipitated lignin relates to the pH and added salt is not completely determined but increasing the salt amount and lowering the pH increases the yield of lignin.

The temperature in the trials did in general not appear to have any significant effect on the result of the precipitation. Gelation is a risk with lignin precipitation as demonstrated, if the precipitation is conducted at room temperature. Precipitation is temperature dependent as demonstrated by experiment 14. Precipitation did not occur until the heating element had been turned on and allowed to heat the solution. The precipitation began at a certain temperature only to speed up past another temperature. These unknown temperatures may be of interest in further studies for more reasons than to know how to avoid gelation. If there is a minimum temperature needed for precipitation to occur that is important information as is the possibility of a higher temperature speeding up the precipitation process. If the temperature has an effect beyond the impact it has on the effective pH is also of interest.

The pH of the solution is extremely important for the precipitation process which is easily demonstrated by any of the titration experiments. A lower pH causes precipitates at a lower salt concentration and vice versa. Lowering the pH after precipitation occurs is quite likely to precipitate more lignin as the addition of more salt does but was not attempted in this study. If the chord distribution changes as the pH lowers is thus unknown.

Evaluation of the PIA

As the PIA is a completely new method under development it was likely to have flaws and undiscovered limitations. Problems can possibly be fixed by changing the operating method, flaws skew the received data while limits determine the possibilities of the system. A working operating method had to be developed and the flaws and limitations identified. A potential issue of the camera may render it unable to distinguish individual particles if the concentration of particles becomes too high and could thus be is a limitation. Finding the boundary of this limitation could be worth to further investigate. The possibility of adjusting the computer and programming may also be of interest if there is unused capability there.

The flow of solution and thus particles is also a factor of possible importance. Is there a preference to size from the flow shifting the results? Many of the particle agglomerates are likely a loose formation of smaller particles attached to each other and this formation could be damaged or break effecting the results. The mixing that takes place is also of interest. The actual level of dilution of the liquid inside the camera house is unknown and as such the concentration of the liquid that the PIA sees and draws its results from. As the dilution pump pumps liquid into the mixing vessel and the circulation circuit the actual ratio of the solutions to each other is unknown. The efficiency of the mixing vessel is also a factor even without the possibility of short circuit.

The method of dosing in some sample liquid produces consistent results with a starting lignin concentration of 5 %. Different pump ratios using dosing and a 5 % lignin solution may have an effect but was not tried due to time constraints. The actual concentration in front of the camera is decidedly lower due to the dilution of the PIA. The actual concentration however is not known.

The difference between the results from the PIA and the FBRM® are quite large but they are consistent in respect to themselves. The FBRM® have been used in earlier experiments and as such is used as a benchmark for the newer PIA. The large difference in between the results makes it difficult to say how accurate the PIAs results are. The two methods are also based on different methodologies which could be what is causing the differences. Particle line up is problematic as the extent of its effect on the PIA result is unknown. Particle line up is functionally impossible for the FBRM®. Thus, any actual difference from the PIA result when comparing the two is distorted. Particle line up may also possibly mask other issues that may be present. The distortion from particle line up is increased by the possibility that particles smaller than 1 µm are responsible for parts of it. As these particles are invisible to the FBRM® they are only seen due to particle line up by the PIA. Thus, the FBRM® and the PIA are not quite measuring the same things and if the reasoning around Figure 8 is correct this could have a large effect.

To proceed with the PIA some issues should be addressed. The pumping ratios should be investigated as should the effect of a wider range of different particle concentrations. The camera and the computer algorithm can likely be optimized further. The FBRM® returns chord counts only while the PIA determines the volume distribution along with other forms of data. Possible comparisons using other investigative methods focusing on the other forms of data is worth doing to determine if the volume distribution alone is skewed but the other results

are fine. In an industrial setting the FBRM® works just fine for the chord distribution leading to the PIAs main attraction being the other type information about the particles it acquires. The type of data of greatest interest is likely to be the aspect ratio which could help determine the shape of the lignin particles.

Conclusions

During this study these are the conclusions that have been drawn:

- FBRM® produces consistent results. The various conditions: temperature, salt type, salt concentration and pH had no visible effects on the chord/particle distribution. The volume, while much easier to shift and disturb, was also quite similar. The chord lengths responsible for the majority in the chord distribution are found at 3-6 µm which had a corresponding volume distribution peaking at 18-22 µm.

- The temperature is an important factor in the precipitation process but after precipitation has occurred the solution is unaffected by the temperature being lowered to room temperature.

- PIA results are significantly different from that of the FBRM®. Early trials produced uneven results which were rarely repeated during the same experiments. This improved with a lowering of the lignin concentration and eventually dosing in the lignin-containing liquid. The PIA is limited by how concentrated the solution that enters it can be. More testing is required to define this limit of lignin concentration in a black liquor but below 5 percent is a reasonable region considering the dilution factor of the dilution liquid in this study.

- PIA is a combination of pumps and a camera with added tubes, making it is a rather complex system. This complexity makes it difficult to understand individual influences on the result. Flow friction and pumping forces may influence the result and is not currently understood and thus suggests further investigation.

- PIA offers other forms of data that can be of interest such as vertical to horizontal aspect ratios which could give insight to the shape of the lignin particles but from a purely particle size and distribution perspective the FBRM® is the superior method now.

Future work

There are two parts of future work possible. One is to continue investigating the precipitation of lignin and the other is to turn the PIA into a reliable experimental machine. When investigating the precipitation, temperature is of interest in order to find the point where gelation starts so it can be avoided. The filtration process depends on particle size and volume which determines the filtration resistance and therefore the volume of washing liquid required. Both the size distribution and the volume distribution are thus of interest and further effect of pH and salt on the volume distribution are of interest. Some suggestions for further PIA developments: try running it normally but keep adding dilution liquid but no lignin solution, to see how retention affects the results. Try the PIA with known dilution and particle solutions to determine the PIA's own overall effect on the result. Find the concentration limitations of the PIA along with accuracy of the camera and computer. How/if the camera and computer program could be improved is beyond the scope of this work. There are also the effects of the tubes and pumps themselves to be considered. Finally, the wagon the PIA is compact and handy from an experimental and transport perspective, however quite difficult to clean and tinker with.

Acknowledgments

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devoted to the issue of stagflation. It is found that with standard monetary feedback rules as currently estimated for the euro area, there is no severe inflation risk. The paper also addresses the issue to what extent there is a short run trade off between inflation and output with an adverse supply shock.

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