



INTERNSHIP AT THE UNIVERSITY OF TENNESSEE – CENTER FOR RENEWABLE CARBON

RESEARCH REPORT

Lignin Yield Determination of Lignocellulosic Feedstocks by Time Series using
Experimental Design

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Abstract

Lignin, a byproduct of the organosolv pretreatment process using lignocellulosic biomass from switchgrass (*Panicum virgatum*), hybrid poplar (*Populus hybrids*), southern yellow pine (*Pinus taeda*) and eucalyptus (*Eucalyptus grandis*) is currently being explored for its potential use in the production of value-added chemicals and biobased polymers. Pretreatment is one of the most expensive processing steps in cellulosic biomass conversion. Optimization is one of the major goals of the biomass-to-ethanol conversion process.

Given the results of several preliminary studies of the organosolv pretreatment process, the following parameters were used: process temperature (130°C, 150°C), fractionation time (120 minutes), sulfuric acid concentration (0.1 M) and feedstocks (switchgrass, hybrid poplar, southern yellow pine, and eucalyptus, latter was used the first time). To gain more information about the lignin yield over process time, samples of black liquor were taken every 15 minutes to show a time curve with the lignin yield distribution.

Based on the results, it can be concluded that the lignin yield increases with higher temperature, which mirrors results from former studies. The highest lignin yield was reached with the new feedstock eucalyptus (28 wt% of the starting feedstock), however impurities can be contained. Furthermore, poplar and switchgrass showed good properties and pine turned out to be difficult to process. In consideration of the run time, a higher temperature caused a much faster lignin extraction. Under severe conditions (150°C), 90% of the lignin from switchgrass and pine were recovered after 60 minutes runtime. A steadier and slower extraction occurred with poplar and eucalyptus feedstocks. In conclusion, the finding that the lignin is not extracted continuously over time may provide a pathway for other researches interested in optimizing the organosolv fractionation process.

Key words: Biorefinery, Lignocellulosic Biomass, Organosolv Fractionation Process, Lignin Content of different Feedstocks

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1. Introduction

Over the last 150 years, fossil fuels have become our most important energy resource. Over the years this has resulted in huge ecologic and economic problems such as the emissions of greenhouse gases in the atmosphere, a very controlled energy market, and a global waste problem with plastics. In addition to this, there is an expected shortage of raw materials, especially oil. It is reasonable to look for alternatives in order to become less dependent on these fossil-based substances. Renewables, especially modern efficient ones, are still just a fragment of our total energy consumption. Due to national energy security, independent fuel supply is intended. Benefits of this are the saved greenhouse gases which lead to global warming, becoming independent from the global energy market by producing our own fuel, and of course using byproducts of this process to produce materials such as plastic substitutes (Robertson et al. 2008; Institute for Energy Research 2013).

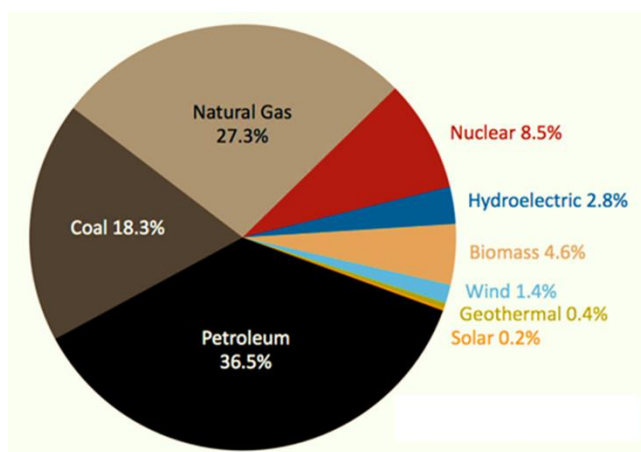


Figure 1. U.S. Energy consumption 2013 (Institute for Energy Research 2013).

The U.S. Congress came to terms in 2004 to replace 30% of the petroleum consumption with cellulosic ethanol by 2030. This will lead to a high demand of lignocellulosic biomass. A study carried out at Oak Ridge National Laboratory (ORNL) determined that there is a demand of 1 billion dry tons of biomass a year, and also proved that is sustainably achievable. It is important to find the proper raw materials and develop reliable processes to convert biomass into the desired products. One of these could be the organosolv fractionation process (U.S. Department of Energy 2013).

Recently, a modified organosolv fractionation process has been developed and implemented at the Center for Renewable Carbon at the University of Tennessee as an improved method for pretreating biomass (Bozell et al. 2011a).

1.1. Objectives

The organosolv fractionation process is a method, where biomass is treated with an organic solvent to separate the material in its single components for further processing. This process requires different parameters including particle size, solvent

composition, solvent temperature, and vessel pressure (Bozell et al. 2011a). Most of these are already known, but because it is a very time-consuming process, it is reasonable to have knowledge of how long it is necessary to treat different biomass. In this series of experiments the main focus was on the lignin yield and the time it takes for the lignin to be extracted. Former studies showed that the temperature has a significant impact on the whole treatment, therefore a lower and higher temperature was included (Astner 2012). There are different types of biomass in use, like switchgrass, poplar, and pine. In addition to this, eucalyptus as a new feedstock was introduced.

2. General Information

The usage of biomass as a renewable resource for products requires vast knowledge of the material itself and the processing. Ideally, you would want a complete utilization of the raw material without any waste.

2.1. Importance of Renewable Materials

Lignocellulosic materials are a promising source of energy because they are the most abundant form of biomass on Earth. This renewable resource is created by photosynthesis, a natural process where only energy in the form of sunlight and water are needed. These kinds of materials are abundant in nature (Pu et al. 2008). In recent years, research has been very busy with the processing of these materials. In particular, the production of bioethanol has attracted much interest. However, the recovery of ethanol is only possible with the cellulose part of the biomass. Commercialization of bio-ethanol depends on the sufficiency of processing conversion rates and low cost inputs. Other substances remain during this process and can be utilized elsewhere. These components mostly form lignin and hemicellulose. The additional use of these can increase the value and make the process more economical. As a result, the development of an integrated biorefinery using sources of renewable carbon as feedstock is widely recognized. With this solution the whole biomass can be utilized for both biochemical and biofuels (Himmel et al. 1999; Wyman et al. 2007).

2.2. Biorefinery

An integrated biorefinery converts lignocellulosic biomass into fuels, value added chemicals, and power. These facilities are similar to petroleum refineries, which produce the same products from crude oil. Production fuels and chemicals are dominated by the conversion of crude oil. However, the utilization and conversion of renewable materials offers a sustainable and independent resource. In addition to this, biorefineries can contribute to enhance economic development and to lower

greenhouse gas emissions. In the United States the concept of these biorefineries is supported by the government. The raw material supply for a biorefinery is vast, coming from a range of sources from the forest, agricultural materials, and residue streams to timber or food production. The development of efficient conversion technologies to produce biochemical and biomaterials is fundamental to the biorefinery concept. Next to the cellulose, which can be used for the production of cellulosic ethanol, lignin, hemicellulose, and other components are recovered from the biomass as an important raw material for many chemical products (Bozell, Petersen 2010; Kazmi 2012).

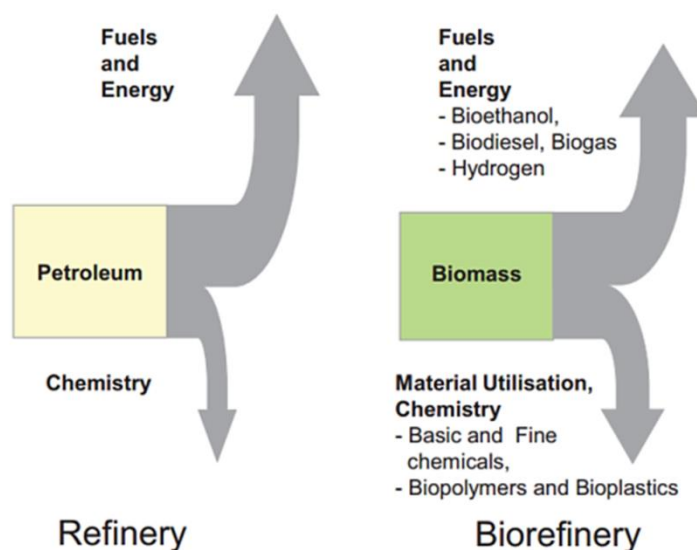


Figure 2. Concept of a biorefinery (Kazmi 2012).

2.3. Chemical Structure of Lignocellulosic Biomass

Optimizing plant biomass for efficient processing requires understanding of plant cell wall structure and function. The cells of lignocellulosic materials are built of the primary and secondary walls and middle lamella. Lignocellulosic biomass is composed of a ternary matrix consisting of cellulose, hemicelluloses, lignin, and smaller amounts of ash and extractives. The secondary cell wall contains the major portion of cellulose; the lignin is concentrated in the middle lamella to bind the neighbored cells together. The distribution of the three major biopolymers in hardwoods, softwoods, and agricultural residues varies. Depending on the species, lignocellulosic biomass is composed of 40-50% cellulose, 15-30% hemicellulose, 15-30% lignin, and 2-5% extractives (Pandey et al. 2009).

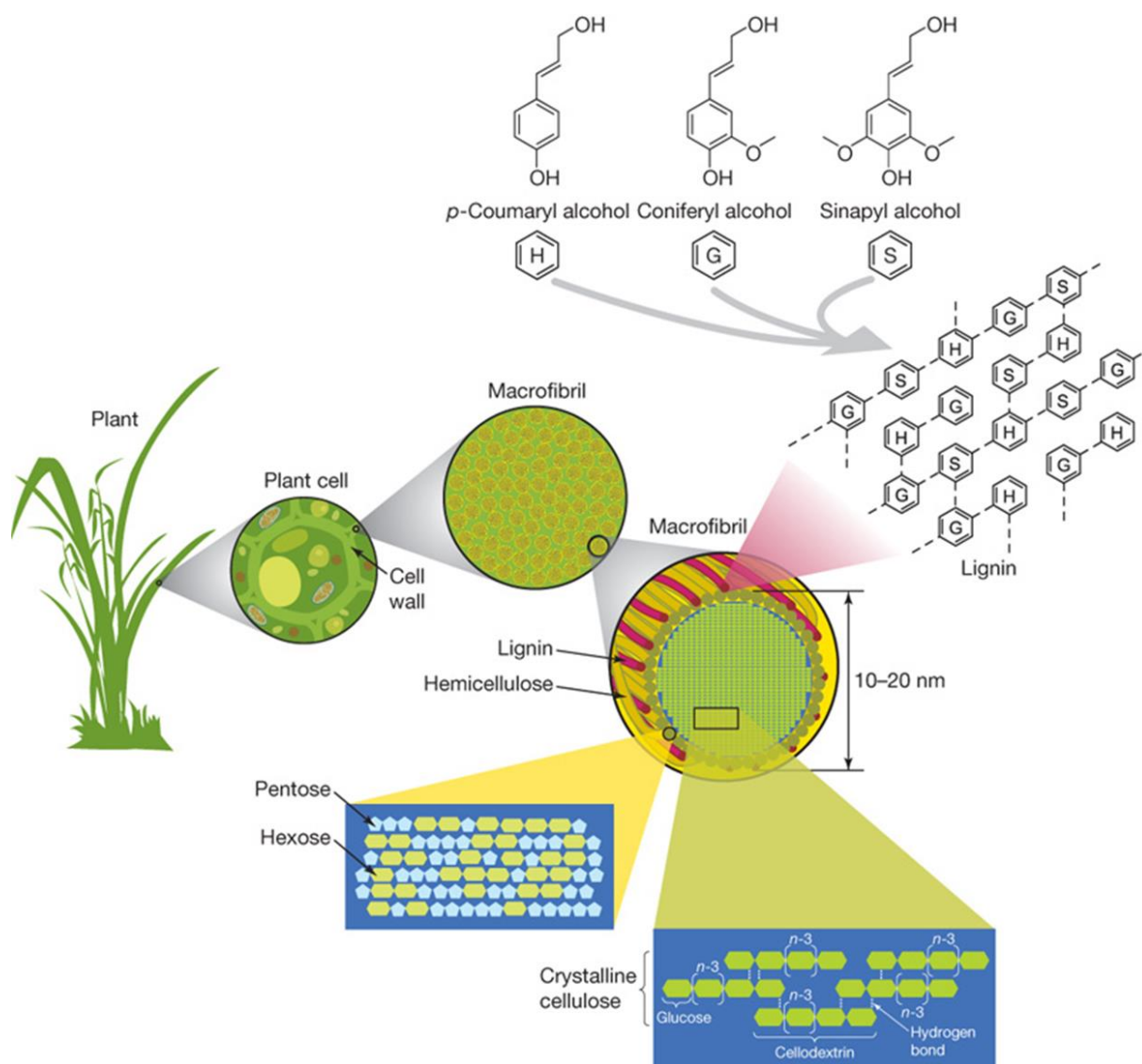


Figure 3. Structure of lignocellulose (Rubin 2008).

Cellulose ($C_6H_{10}O_5$)_n is an organic compound. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of β (1-4) linked D-glucose units. It is an important structural component of the primary cell walls of all green plants and is the most abundant organic polymer on Earth. Hemicellulose is a group of complex carbohydrates that surround the cellulose fibers of plant cells. The most common hemicelluloses contain xylans, an uronic acid and arabinose (Yang et al. 2007; Pandey et al. 2009).

Lignin is a class of complex organic polymers which is particularly important in the formation of cell walls. Lignin is composed of three major phenolic components, namely *p*-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S). It is the second most abundant natural polymer in the world. Between 40 and 50 million tons per annum are produced worldwide as a mostly non-commercialized waste product (Rubin 2008).

3. Material and Methods

This chapter describes the materials used in this research and the work stages. An essential part forms the different raw materials and the solvent fractionation of these. Furthermore, the procedure is defined in the preparation of lignin and the other byproducts.

3.1. Feedstock

In this study, four different types of biomass were used, including switchgrass, hybrid poplar, southern yellow pine, and eucalyptus. With the exception of the latter, the use of these feedstocks has already been tested for the process and has proved to be suitable.

3.1.1. Switchgrass (*Panicum virgatum*)

Panicum virgatum, commonly known as switchgrass, is a perennial warm season bunch grass. The plant is 3 to 5 feet tall and spreads from short, stout rhizomes. The stem is covered with 1 to 3 feet long leaves with a prominent midrib. The seed head is an open, spreading panicle. It is native to North America, where it grows in the continental United States. Switchgrass is a versatile and adaptable plant. It can grow and even thrive in many weather conditions, lengths of growing seasons, soil types, and land conditions. However, to persist several years and produce economical biomass yields it has certain requirements for growth. Most important is a warm climate during growing season. It performs best on shallow and droughty soils. As livestock, the plant is important to stabilize soil from erosion and in the farming industry to control the nutrient budget of farmland or as a windbreak in crop fields. The high biomass yield of the plant has resulted in the use of switchgrass in several bioenergy conversion processes, including cellulosic ethanol production, biogas, and direct combustion for thermal energy applications (Carter 2011).



Figure 4. Switchgrass field (left) and dry feedstock (right).

Alamo switchgrass used for this series of experiments is harvested in East Tennessee. The air-dried material was comminuted in a hammer mill and screened (mesh size 0.187 & 0.0937 inch) to give material with uniform size. Moisture content was determined on average to be 8.33% by weighing the biomass before and after drying in an oven at 105°C for 12 h. Results from compositional analysis of the biomass are published in a preliminary study (Bozell et al. 2011b).

3.1.2. Hybrid Poplar (*Populus hybrids*)

Many hybrid clones between *Populus* have been planted in the Eastern to Midwest United States. These deciduous trees get 40 to 60 feet tall and grow very fast but often lack the cold and drought hardiness of the native cottonwood. Most species require warm regions and a moist site. It is commonly grown in short-rotation plantations (10 to 20 years) as firewood, for energy production biomass, or for pulp production (Pearson et al. 2010).

Poplar chips used for this study had dimensions of approximately 4 cm² and thicknesses of 0.5-1 cm and were purchased from Oak Ridge Hardwoods, Oak Ridge, Tennessee. The wood chips were air dried (7.7%), hammer milled, and screened to get uniform particle size (mesh size 0.187 & 0.0937 inch). Compositional analysis results were used from former studies (Davison et al. 2005).

3.1.3. Southern Yellow Pine (*Pinus taeda*)

Pinus Taeda is a native, evergreen conifer with a long, straight, cylindrical bole. The plant grows rapidly, and is 90 to 110 feet tall. It is the leading commercial timber species in the southeastern United States. Young, open-grown pines grow 2 to 3 feet in height annually. Most harvested pines are under 50 years old and were used for lumber and pulpwood production (Carey 2015).

Pine chips used for this study had dimensions of approximately 4 cm² and thicknesses of 0.5-1 cm and were from Oak Ridge, Tennessee. These chips were hammer milled and screened (mesh size 0.187 & 0.0937 inch). Moisture content was determined with 9.52%. A composition analysis of *Pinus taeda* is made in different former studies (Pasquini et al. 2005).

3.1.4. Eucalyptus (*Eucalyptus grandis*)

Eucalyptus is a tree species with many different subspecies. It is originally from Australia, but was introduced to Florida and the Southeastern states. It is commonly grown in plantations. *Eucalyptus grandis* grows as a straight and tall forest tree, reaching around 160 feet tall. At proper conditions with a very warm and humid climate the tree grows extremely fast. It has been successfully tested for pulpwood and fuel, and its wood has potential for poles, pallets, veneer, and other products.

Eucalyptus is a relatively new feedstock for the usage in biorefineries (Meskimen, Francis 2012).



Figure 5. Coarse eucalyptus chips with impurities (left), milled material after hammer mill (middle) and screened feedstock (right).

The wood chips used in this study were from ArborGen Inc., Alabama, from trees just under three years old and cut during the summer. The wood chips were contaminated with a lot of bark, which had to be sorted out manually. After milling the wood chips in a hammer mill the material was screened (mesh size 0.187 & 0.0937 inch). During this process the remaining bark could be deposited. Moisture content was determined on average to be 10%. For this feedstock, no compositional analysis was made, therefore the data from a related study was taken (Emmel et al. 2003).

3.2. Organosolv Fractionation Process

The organosolv fractionation process is a pulping technique that uses an organic solvent to solubilize lignin and hemicellulose. It has been considered in the context of both pulp and paper manufacture and biorefining for subsequent conversion of cellulose to fuel ethanol. The process was invented by Theodor Kleinert in 1968 (Baskar et al. 2012).

3.2.1. Solvent Composition

A solvent mixture consisting of methyl-isobutyl ketone (MIBK), ethyl-alcohol (Ethanol 190 proof), and deionized water (DI-Water) was used for the pretreatment of the lignocellulosic biomass. As a catalyst, sulfuric acid (96% H_2SO_4) was added in the concentration of 0.1M. This so called “minus 1 Solvent” was found to be the most efficient composition for the solvent fractionation process (Bozell et al. 2011a).

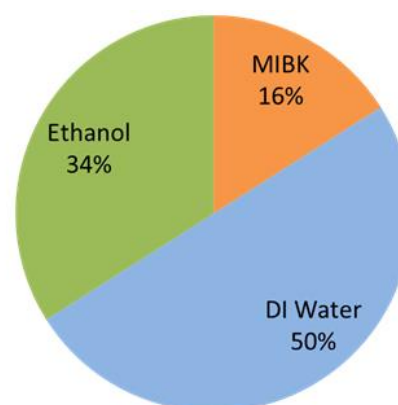


Figure 6. Composition of solvent for organosolv fractionation (Bozell et al. 2011a).

3.2.2. Reactor

The University of Tennessee Center for Renewable Carbon has been operating a solvent fractionation process for several years. The main unit is the vessel where the biomass and the solvent are and the fractionation occurs. The fractionation system works in batch flow-through mode and is designated to operate with pressure up to 1,000 psi and temperatures up to 200°C. The continuous solvent flow is controlled by an air driven pump combined with an automated valve. On the bottom of the reactor the black liquor is recovered. The non-soluble part of the biomass remains in the reactor. System operations are controlled and monitored using Lab-VIEW 8.6 software (Astner 2012).

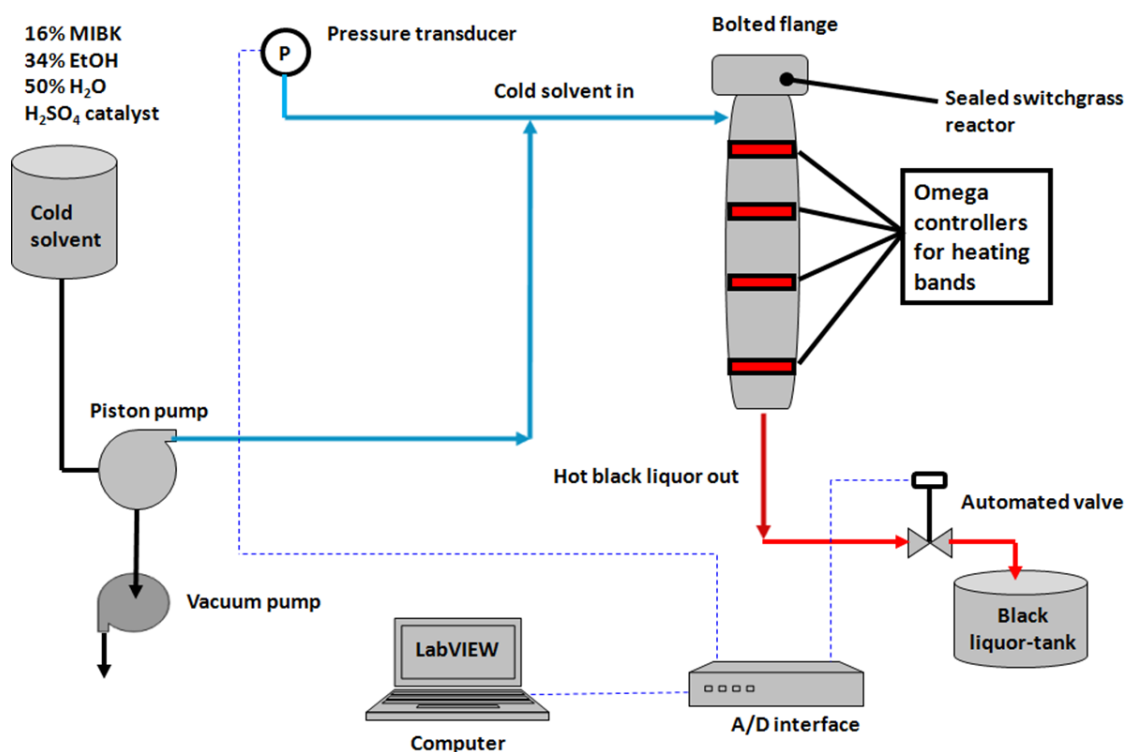


Figure 7. Reactor layout and flow diagram (Bozell et al. 2011a).

3.2.3. Run Matrix

Over the course of this experiment, a total of 8 reactor runs were conducted. The four feedstocks switchgrass, poplar, pine, and eucalyptus were used. In addition, the temperature greatly affects the whole process, which is why each low and high temperature was tested. The 8 different runs with feedstocks and conditions are listed in table 1.

Table 1. Run matrix with feedstocks and conditions.

Run Number / Internal Number	Feedstock	Conditions			
		Solvent	Acid level	Runtime	Temperature
1 / CRC 83	Switchgrass	minus 1	0.1M	120 min	150°C
2 / CRC 85	Switchgrass	minus 1	0.1M	120 min	130°C
3 / CRC 90	Poplar	minus 1	0.1M	120 min	150°C
4 / CRC 95	Poplar	minus 1	0.1M	120 min	130°C
5 / CRC 96	Pine	minus 1	0.1M	120 min	150°C
6 / CRC 98	Pine	minus 1	0.1M	120 min	130°C
7 / CRC 99	Eucalyptus	minus 1	0.1M	120 min	130°C
8 / CRC 100	Eucalyptus	minus 1	0.1M	120 min	150°C

3.2.4. Fractionation Process

The fractionation process is divided into 5 phases, the vacuum, filling, heating up, solvent flow, and shutdown.

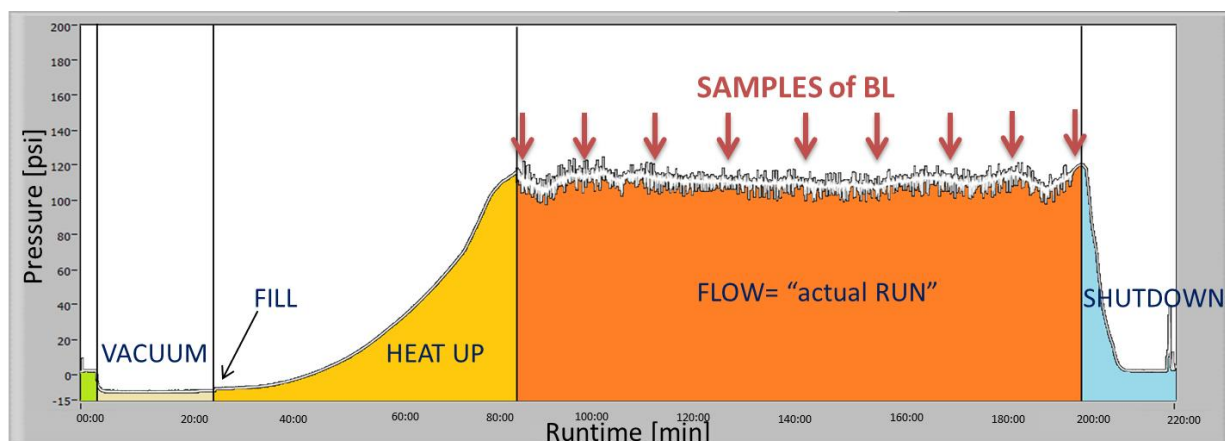


Figure 8. Pressure history in the reactor over runtime with different phases.

The reactor was charged with a perforated Teflon basket containing the specific feedstock (400 g moist). In the first phase of the process a vacuum was applied at -11 psi for about 20 minutes. This leads to a degasification of the feedstock and improves penetration with the organic solvent in the next step. Next, the valve to the solvent tank was opened so that the reactor fills up. When the reactor was totally filled the vacuum pump was shut off, and all valves are closed. The reactor is equipped with four heater bands which brings the vessel at the operation temperature. Usually it takes about 45 to 60 minutes to reach a core temperature of 130 or 150°C. Simultaneously, a pressure was built up by the heating. The

equilibrium pressure increases exponentially as a function of temperature (65 psi at 130°C or 120 psi at 150°C). A relief valve ensures that the pressure doesn't increase too high causing an imbalance inside the reactor. As soon as the desired core temperature was reached the solvent pump was turned on to allow fresh solvent to be pumped in the vessel. An average flow rate of 55-75 ml/min should be sought to ensure the comparability between the runs. The used solvent which contains the soluble parts of the biomass was recovered at the bottom of the reactor. From this point the process continuous for 120 minutes. During this period, 200 ml samples of the extracted liquid were taken every 15 minutes. This liquid is the so called "black liquor" that contains most of the hemicellulose and lignin. After expiration of the run time the reactor was shut down. This means that the heating bands and the pump were turned off and the remaining solvent was drained. Next to the black liquor, there was a non-soluble part that remains solid in the reactor. Depending on the degree of decomposition this was mainly cellulose.

3.3. Workup

After each reactor run there were two main products, the black liquor containing the solved hemicellulose and lignin, and the solid cellulose. These components have to be retreated for further use.

3.3.1. Black Liquor and Black Liquor Samples

After each run two fractions were further processed to black liquor. On one hand, the 9 samples which were taken over time, on the other hand, a large pot of remaining black liquor. The preparation of these was carried out according to the same principle.

As the black liquor contains both – hemicellulose and lignin – the next step was the separation of these two components. Before the actual separation was carried out, the black liquor was filtered with a coarse filter paper (filter size 417) using a Buchner funnel to remove solid impurities like small pieces of biomass. Thereby the liquid amount was measured as an important indicator for the run. Lignin and hemicellulose are dissolved in ethanol and MIBK, which is why these two components of the solvent mixture have to be removed. This was done by evaporation on a rotary evaporator at vacuum and higher temperature (-90 psi, 50°C). Through these conditions the volatile liquids evaporate first, leaving water and solid components.



Figure 9. Reactor main outlet with pot and bypass for sample taking.

In the next step, this liquid was filtered again (filter size 413) to isolate the solid lignin from the remaining water. The largest part of the hemicellulose was contained in this yellow to orange filtrate. For further analysis of the hemicellulose a 100 ml sample of the filtrate is frozen and stored. The lignin obtained still contains residual moisture, so it was dried overnight in a vacuum oven at 80°C and -25 psi. The dry and powdery lignin was weighed and stored for further analysis.



Figure 10. Buchner filtration of the lignin (left) and dry lignin powder (right).

The workup was made differently to the common procedure. Instead of a phase separation in organic and aqueous phase with NaCl or H₂O, the whole black liquor was further processed. The advantage of this kind of workup was to save a lot of time and resources for the separation, but the lignin is not pure because there are little contaminates of solvent and hemicellulose. The further process would be to wash the lignin and determine the Klason lignin, but this was not part of this study. To simplify and accelerate the whole workup, the dry lignin with impurities was directly weighed to determine the approximate yield (Astner 2012).

3.3.2. Cellulose Recovery

After unloading the reactor, the remaining biomass was mixed with deionized water to stop the decomposition due to the solvent. In addition, it was necessary to wash this material to remove any residues of the solvent. A blender was used to fiberize the cellulose for a better removal of the solvent. After washing for about one to two hours and squeezing out the majority of the water, the cellulose was weighed and samples for the determination of the moisture content were taken. The cellulose was then stored in a freezer for further processing.

4. Results and Discussion

This chapter describes the results of the experiments and further analysis that have been made. Detailed information can be found in the appendix.

4.1. Total Lignin Yield

The total lignin yield describes the amount of lignin which was generated per run, including the major fraction and the individual samples. The theoretical lignin content depends heavily on the feedstock because every type of biomass has a different composition of cellulose, hemicellulose, and lignin. These values can be determined with compositional analysis or from the literature. The listed lignin contents include impurities of hemicellulose, solvent residues, and other secondary wood components. That explains the very high lignin yields determined in some cases.

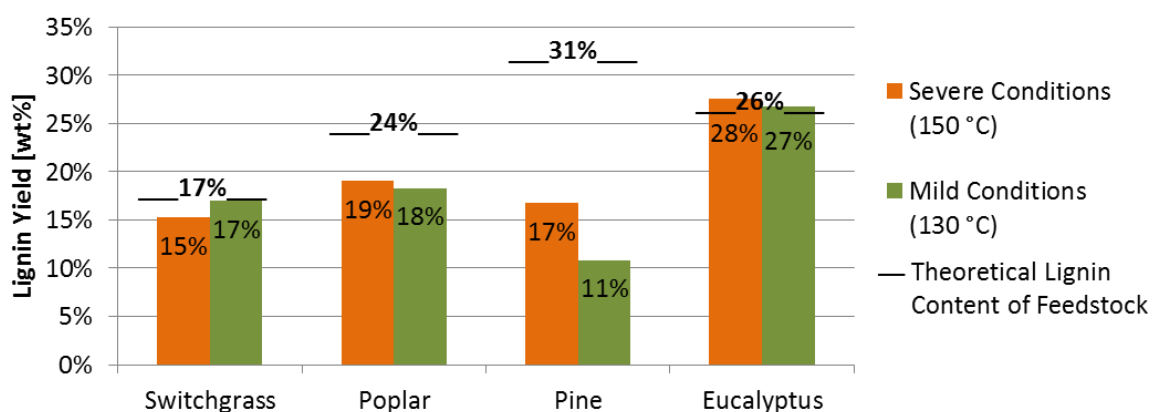


Figure 11. Comparison of the total lignin yields referring to the mass of the starting feedstock.

In general it can be said that the organosolv fractionation process works very well with the used feedstocks. The temperature has a significant impact on the lignin yield. Switchgrass has a relative lignin content of 17%; both values reached during the runs come very close to this. Especially with higher temperatures, theoretically all of the contained lignin could be extracted. Similar to this, eucalyptus could be processed very successfully, but the reached lignin yield is higher than the theoretical content, which can recognize that this material is contaminated. Furthermore, poplar is very suitable, since here a high yield was achieved. Pine in contrast is very difficult to process and less lignin could be extracted. Coniferous trees are very hard to process in this context, however the theoretical lignin content is much higher than at hardwoods.

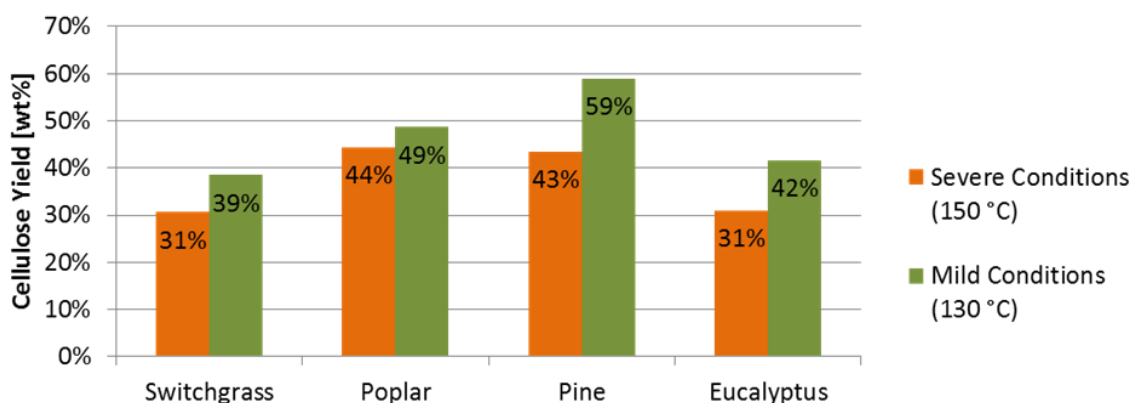


Figure 12. Comparison of the total cellulose yields referring to the mass of the starting feedstock.

In comparison to this is the cellulose yield of the runs. There is a correlation between lignin and cellulose yield. When lignin yield gets higher, amount of recovered cellulose is lower and vice versa. Also this material is contaminated and the purity had to be determined.



Figure 13. Lignins of different feedstocks and run conditions.

Depending on the feedstock and conditions, the color of the lignin is very different. In general, the lignin is always darker when the temperature is higher. Former studies showed that this lignin has also a higher purity (Astner 2012). Switchgrass and poplar are both very dark-brown. Pine's lignin is very bright and a bit sticky, probably due to a high contamination with resin. Eucalyptus has a very red lignin, which was also the color of the black liquor, which can be caused from a high amount of tannins and other secondary wood components.

4.2. Lignin Yield over Runtime

The lignin yield over the runtime was determined based on the 200 ml samples of black liquor which were taken every 15 minutes during the runtime. Each of the 9 samples was worked up separately to avoid cross-contamination. The individual fractions were stored for further investigation and analysis. The lignin yield of each sample was determined gravimetrically. Because the amount of lignin is very low with these small samples, the whole pan with dried filter and lignin was weighed and the difference to the tare weight calculated. These values are to be expected a little too high as in reality, as these lignins are also contaminated.

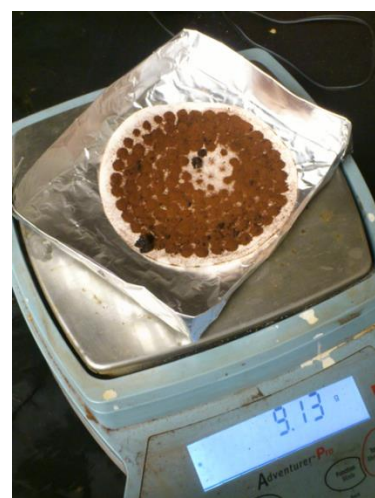


Figure 14. Weighing a lignin sample.

4.2.1. Switchgrass

The following chart shows the lignin yield of switchgrass over the runtime in 15 minutes steps. The yield of every sample in grams is shown in the bars, each for a high and low temperature. The line shows the cumulative lignin yield in weight percent of the total sample. The percentages refer to the sum of the samples and do not show the total amount of lignin in the feedstock regarding the composition analysis.

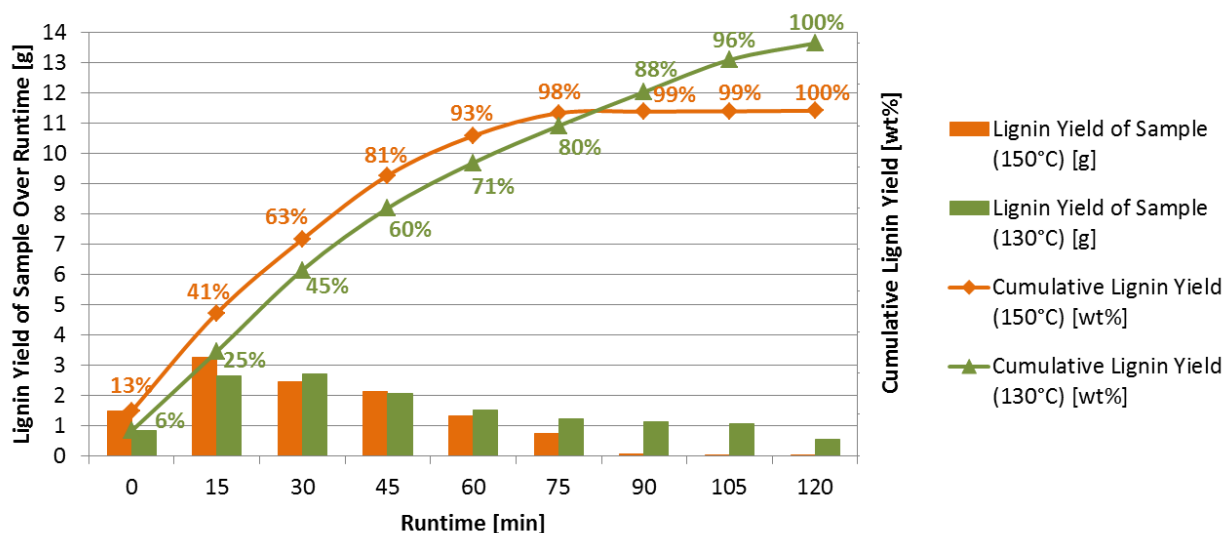


Figure 15. Switchgrass lignin yield in consideration on the samples over runtime.

The run with switchgrass at 150°C has a lower total lignin yield (11.41g = 100%) compared to the run at 130°C where a higher amount of lignin was attained (13.64g = 100%). Interestingly, almost 95% of the recovered lignin is already recovered after 60 minutes and then there is no further significant increase. At these conditions, it would be not necessary to keep the process running for 120 minutes. In the remaining half of the time, a lot of energy and resources like solvent are wasted, resulting in unnecessary costs and making the process uneconomical. With lower temperature the extraction is slower and steadier over the runtime. The lignin yield is much more distributed over the runtime. It is unusual that the lignin yield is higher with lower temperature. This can be explained by a high degree of contamination of the lignin. An analysis of the lignin would give indication.

Because of the big surface of the particles, it is easy for the solvent to penetrate. Switchgrass shows a very high yield with an almost complete lignin extraction, but the absolute amount of lignin in this feedstock is very low. So much more raw material would be needed to obtain the same amount of lignin compared to other common feedstocks.

4.2.2. Poplar

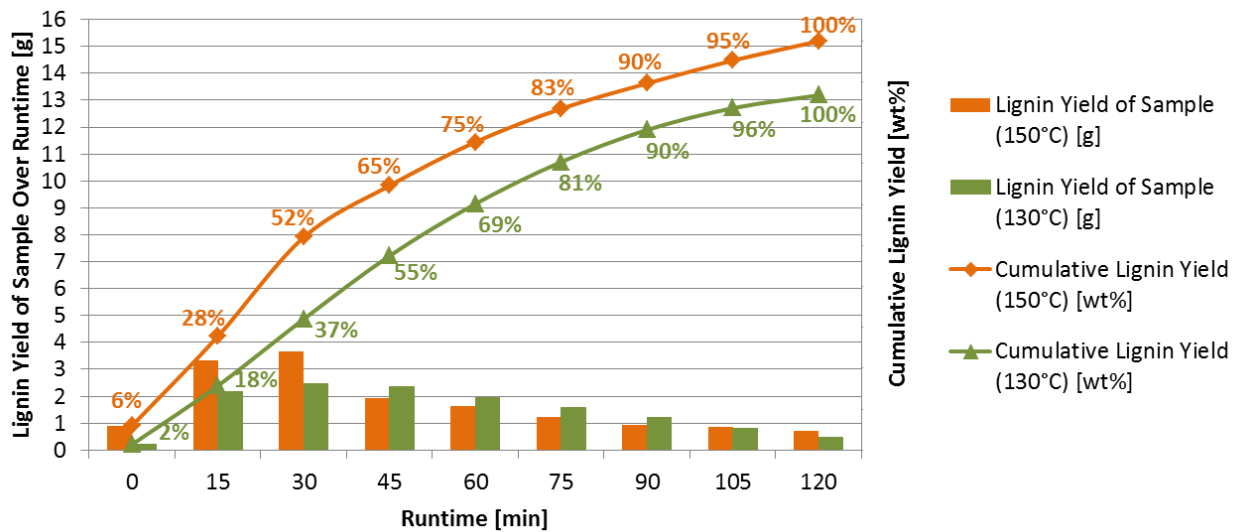


Figure 16. Poplar lignin yield in consideration on the samples over runtime.

Poplar behaves very constant and predictable. A higher temperature causes a higher lignin yield (15.20g = 100%), and at a lower temperature less lignin could be extracted (13.19g = 100%). In total, with mild conditions the lignin yield was 13% lower, but the process is steadier. At 150°C, in the first 30 minutes a very fast extraction happens whereby half of the received lignin was extracted. After this point, both runs behave quite similar. Therefore, poplar would be suitable for the organosolv fractionation process also in an industrial scale because with a relatively low material input a large amount of lignin can be recovered.

4.2.3. Pine

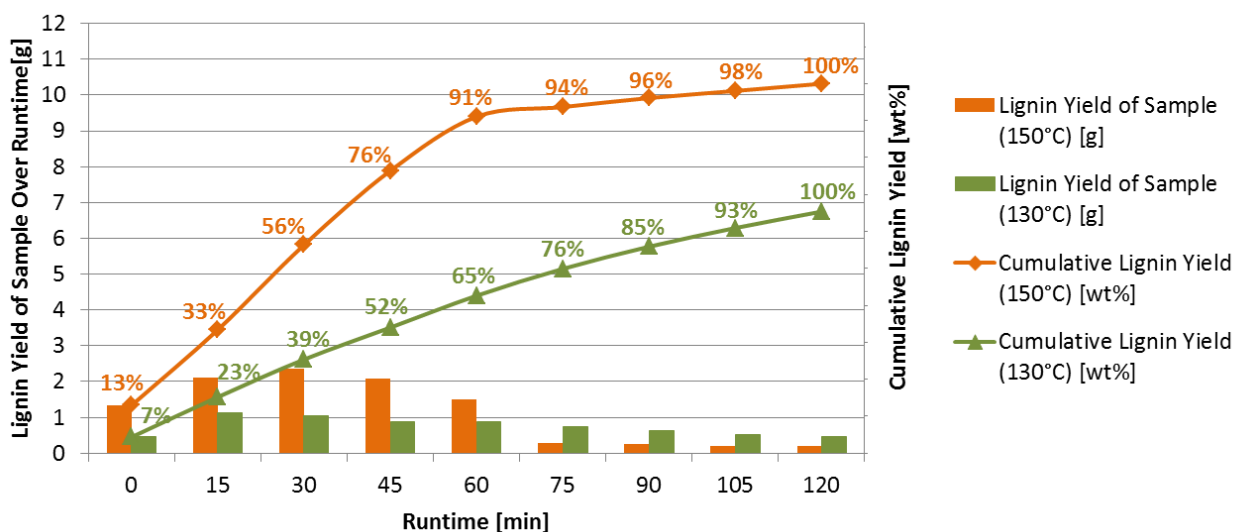


Figure 17. Pine lignin yield in consideration on the samples over runtime.

Coniferous trees like pine are very difficult to process because of their physical structure. In general the lignin yield is very low. With pine as feedstock for the organosolv fractionation process, the temperature has a huge impact on the extraction. Between the two conditions at 150°C (10.32g = 100%) and 130°C (6.75g = 100%) there is a difference in the final lignin yield of 35%. When the process temperature was 150°C, 90% of the generated lignin was extracted after 60 minutes. In the last half of the runtime the process proceeded very slowly. With mild conditions an almost linear extraction occurs, but the process is very slow and inefficient.

4.2.4. Eucalyptus

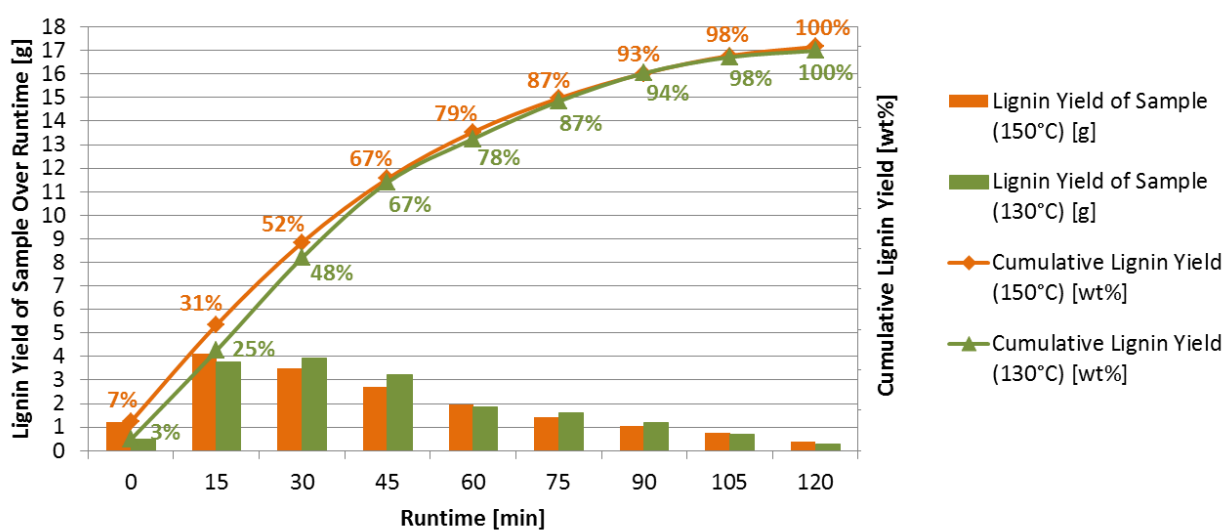


Figure 18. Eucalyptus lignin yield in consideration on the samples over runtime.

Eucalyptus as a new feedstock for the organosolv fractionation process is very interesting. There is almost no difference between the two temperatures in the extraction speed, and the final lignin yield is similar (150°C: 17.16g = 100%; 130°C: 16.99g = 100%). In both cases the process proceeded fast and steady.

5. Conclusions

In consideration of all the research data, it can be verified that higher temperature causes a higher lignin yield. Temperature has a high impact on the organosolv fractionation process (Astner 2012; Bozell et al. 2011a). Pine as a coniferous species is the most difficult of the used feedstock for this process. Switchgrass is especially easy for extracting lignin because of a high surface and a good penetration of the solvent, but the absolute amount of lignin in this feedstock is very low. Therefore poplar would be suitable for the organosolv fractionation process at an industrial scale because with a relatively low material input, a large amount of lignin can be recovered. A big surprise is the eucalyptus with a very high lignin yield, but at this

point further testing will need to happen to be able to say anything definitively about the properties of this lignin.

In consideration of the runtime, a higher temperature causes a much faster lignin extraction. This data is consistent with results from similar studies (Delbeck 2012). After a certain amount of time the lignin extraction is so slow and in such a small scale that it is not worth the small lignin yields to keep the process running. However, it should be noted that there are significant differences between the feedstock. With the feedstocks switchgrass and pine, most of the lignin is already removed after 60 minutes under severe conditions (150°C). In contrast, poplar and eucalyptus behave very similar and constant regardless of the conditions.

5.1. Future Research

This research shows a small section of this complex topic. There are still many subjects to look at. In this context, it has to be checked if the lignin is still usable for further research. Because of the different workup, the purity of the lignin is not that high. Researching the chemical structure of the lignins would be interesting.

Currently there is a paper at the University of Tennessee, Center for Renewable Carbon in process about this topic. Thereby the focus is on the chemical structure of the lignin fractions with pine as feedstock under specific conditions. This analysis would also be interesting in context with this research with different feedstocks and temperature conditions. Therefore a Klason lignin analysis of the entire lignin must be performed. To determine the properties, a differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the lignin could be performed. These experiments would provide important information for the use of carbon fiber spinning. Also the cellulose is an important byproduct of the organosolv fractionation process. This material can also be used for further analysis. Further research using Eucalyptus as the feedstock would also be very interesting because the lignin yield looks very promising.

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Appendix

Table 2. Different fractions after screening of the milled chips.

	Switchgrass		Poplar		Pine		Eucalyptus	
Total	5.355 kg	100 %	5.106 kg	100 %	5.986 kg	101 %	3.623 kg	100 % (Bark)
1. Fraction	0.003 kg	0 %	0.076 kg	1 %	0.032 kg	1 %	0.008 kg	0 % 0.020 kg
2. Fraction	0.342 kg	6 %	1.275 kg	25 %	1.754 kg	29 %	0.953 kg	26 % 0.030 kg
3. Fraction	3.365 kg	63 %	1.985 kg	39 %	2.553 kg	43 %	1.774 kg	49 % 0.030 kg
4. Fraction	1.645 kg	31 %	1.770 kg	35 %	1.693 kg	28 %	0.888 kg	25 % -
MC [%]	8.33		7.70		9.52		10.04	
Mesh size								
1. Fraction: No.4; 4.75 mm; 0.187 inch								
2. Fraction: No.8; 2.36 mm; 0.0937 inch								
3. Fraction: No.20; 0.850 mm; 0.0331 inch								
4. Fraction: Finer material and dust								

Table 3. Workup datasheet for run CRC 83.

Run No.	CRC 83		Black Liquor Workup				
Feedstock	400g Switchgrass fine		BL Pot [ml]	5470			
Conditions	-1/150°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	7270			
Average flow [ml/min]	56.54		Aqueous Rotavap Pot [ml]	2650			
Solid to Liquid Ratio	23.5		Aqueous Rotavap Samp.[ml]	615			
			Total Aqueous [ml]	3265			
Lignin Yield of Run			Cellulose Yield of Run				
Lignin Remains Pot1 [g]	0.68		Feedstock	SG fine			
Lignin Remains Pot2 [g]	0.35		Mass of Feedstock [g]	400			
Lignin Remains Filter	2.67		MC of Feedstock [%]	8.3			
Lignin Samples [g]	11.41		Dry Mass of Feedstock [g]	369.23			
Lignin BL [g]	41.13		Washed Cellulose [g]	524.29			
MC of Lignin [%]	10.1		MC of Cellulose [%]	364			
Total Lignin Yield [g]	56.24		Dry Mass of Cellulose [g]	112.96			
Total Lignin Yield [%]	15.2						
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	8	200	75	1.47	13%	13%
2	15	02:30	200	75	3.25	28%	41%
3	30	02:30	200	75	2.44	21%	63%
4	45	02:30	200	60	2.11	18%	81%
5	60	02:30	200	70	1.31	11%	93%
6	75	02:30	200	65	0.75	7%	99%
7	90	04:00	200	50	0.05	0%	100%
8	105	04:00	200	75	0.01	0%	100%
9	120	04:00	200	70	0.02	0%	100%

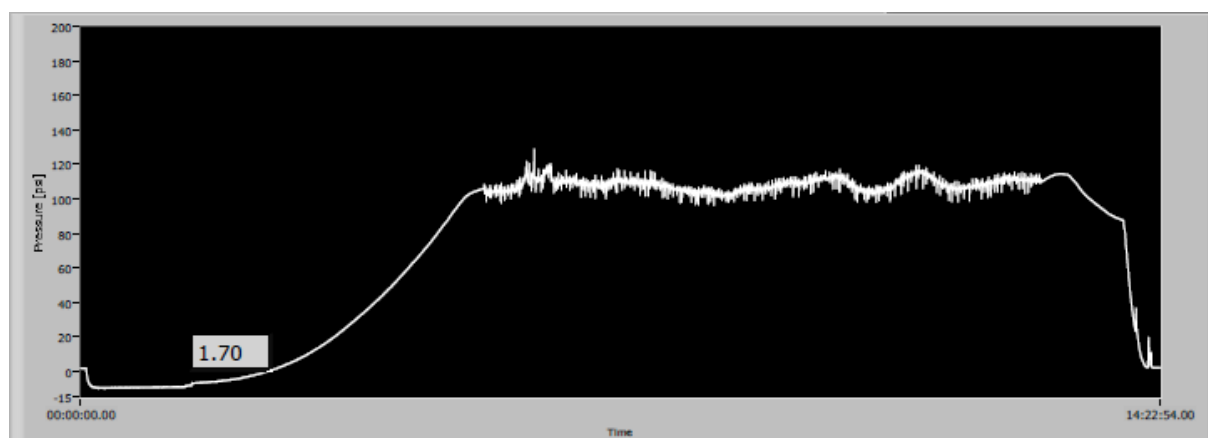


Figure 19. Pressure diagram for run CRC 83.

Table 4. Workup datasheet for run CRC 85.

Run No.	CRC 85		Black Liquor Workup				
Feedstock	400g Switchgrass fine		BL Pot [ml]	6610			
Conditions	-1/130°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	8410			
Average flow [ml/min]	57.15		Aqueous Rotavap Pot [ml]	2650			
Solid to Liquid Ratio	24.4		Aqueous Rotavap Samp.[ml]	725			
			Total Aqueous [ml]	3375			
Lignin Yield of Run			Cellulose Yield of Run				
Lignin Remains Pot1 [g]	0.99		Feedstock	SG fine			
Lignin Remains Pot2 [g]	0.48		Mass of Feedstock [g]	400			
Lignin Remains Filter	1.84		MC of Feedstock [%]	8.3			
Lignin Samples [g]	13.64		Dry Mass of Feedstock [g]	369.23			
Lignin BL [g]	45.81		Washed Cellulose [g]	790.45			
MC of Lignin [%]	7.1		MC of Cellulose [%]	456			
Total Lignin Yield [g]	62.76		Dry Mass of Cellulose [g]	142.20			
Total Lignin Yield [%]	17.0						
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	10:00	200	75	0.82	6%	6%
2	15	03:30	200	80	2.63	19%	25%
3	30	03:00	200	75	2.69	20%	45%
4	45	03:00	200	80	2.05	15%	60%
5	60	03:00	200	80	1.5	11%	71%
6	75	03:00	200	90	1.22	9%	80%
7	90	05:30	200	75	1.12	8%	88%
8	105	05:30	200	90	1.06	8%	96%
9	120	05:00	200	80	0.55	4%	100%

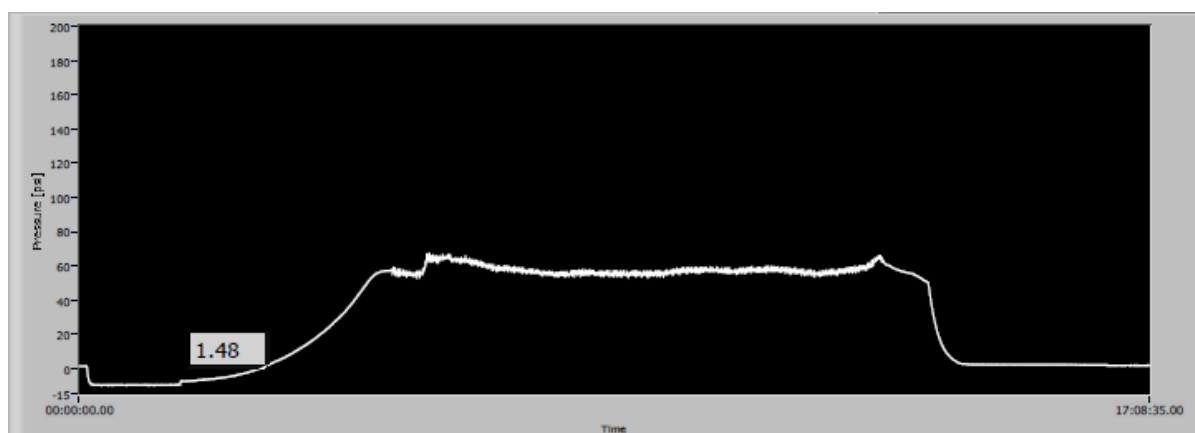


Figure 20. Pressure diagram for run CRC 85.

Table 5. Workup datasheet for run CRC 90.

Run No.	CRC 90		Black Liquor Workup				
Feedstock	400g Poplar fine		BL Pot [ml]	7010			
Conditions	-1/150°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	8810			
Average flow [ml/min]	55.78		Aqueous Rotavap Pot [ml]	3400			
Solid to Liquid Ratio	24.6		Aqueous Rotavap Samp.[ml]	695			
			Total Aqueous [ml]	4095			
Lignin Yield of Run			Cellulose Yield of Run				
Lignin Remains Pot1 [g]	1.38		Feedstock	Poplar fine			
Lignin Remains Pot2 [g]	0.26		Mass of Feedstock [g]	400			
Lignin Remains Filter	0.1		MC of Feedstock [%]	7.7			
Lignin Samples [g]	15.2		Dry Mass of Feedstock [g]	371.40			
Lignin BL [g]	53.75		Washed Cellulose [g]	682.15			
MC of Lignin [%]	13.6		MC of Cellulose [%]	314			
Total Lignin Yield [g]	70.69		Dry Mass of Cellulose [g]	164.65			
Total Lignin Yield [%]	19.0						
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	03:00	200	75	0.91	6%	6%
2	15	03:00	200	80	3.32	22%	28%
3	30	03:20	200	80	3.68	24%	52%
4	45	03:20	200	75	1.92	13%	65%
5	60	03:20	200	80	1.62	11%	75%
6	75	03:20	200	75	1.24	8%	83%
7	90	03:40	200	75	0.94	6%	90%
8	105	03:30	200	80	0.85	6%	95%
9	120	03:20	200	75	0.72	5%	100%

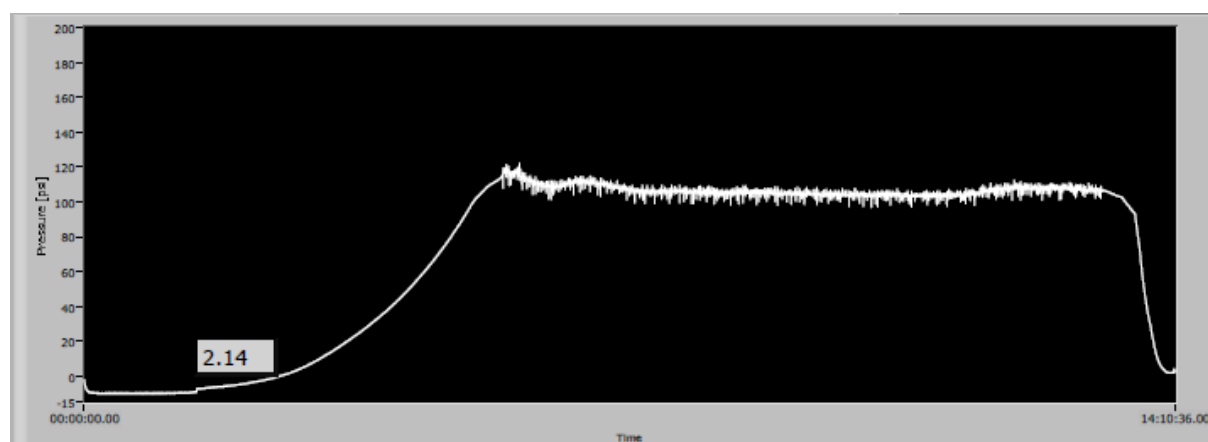


Figure 21. Pressure diagram for run CRC 90.

Table 6. Workup datasheet for run CRC 95.

Run No.	CRC 95		Black Liquor Workup				
Feedstock	400g Poplar fine		BL Pot [ml]	6260			
Conditions	-1/130°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	8060			
Average flow [ml/min]	57.07		Aqueous Rotavap Pot [ml]	2780			
Solid to Liquid Ratio	24.9		Aqueous Rotavap Samp.[ml]	670			
Lignin Yield of Run			Total Aqueous [ml]	3450			
Lignin Remains Pot1 [g]	11.28		Cellulose Yield of Run				
Lignin Remains Pot2 [g]	2.64		Feedstock	Poplar fine			
Lignin Remains Filter	3.83		Mass of Feedstock [g]	400			
Lignin Samples [g]	13.19		MC of Feedstock [%]	7.7			
Lignin BL [g]	37.07		Dry Mass of Feedstock [g]	371.40			
MC of Lignin [%]	38.0		Washed Cellulose [g]	897.3			
Total Lignin Yield [g]	68.01		MC of Cellulose [%]	396			
Total Lignin Yield [%]	18		Dry Mass of Cellulose [g]	180.83			
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	06:00	200	60	0.21	2%	2%
2	15	02:30	200	85	2.18	17%	18%
3	30	02:50	200	75	2.48	19%	37%
4	45	02:40	200	75	2.35	18%	55%
5	60	02:40	200	75	1.93	15%	69%
6	75	02:40	200	80	1.56	12%	81%
7	90	02:40	200	70	1.19	9%	90%
8	105	02:50	200	75	0.81	6%	96%
9	120	03:30	200	75	0.48	4%	100%

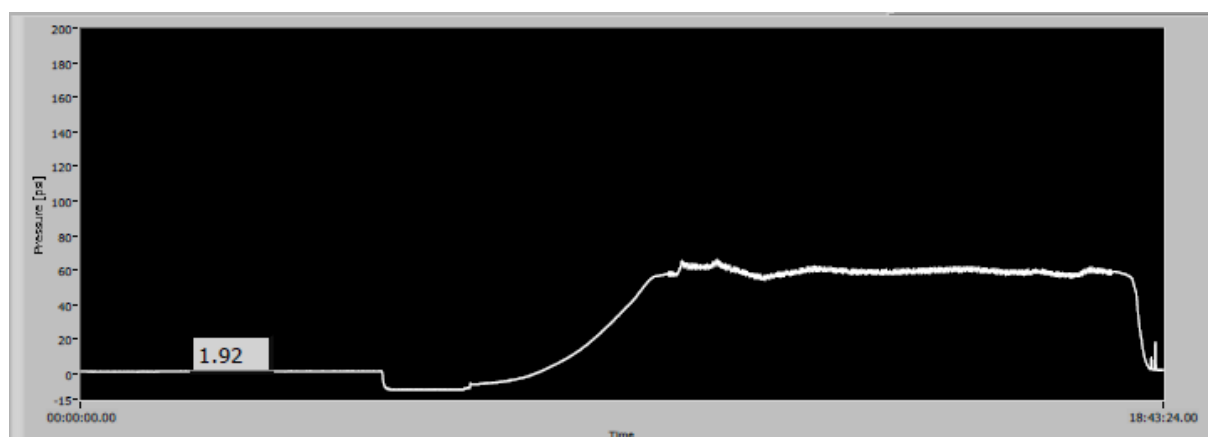


Figure 22. Pressure diagram for run CRC 95.

Table 7. Workup datasheet for run CRC 96.

Run No.	CRC 96			Black Liquor Workup			
Feedstock	400g Pine fine			BL Pot [ml]	5860		
Conditions	-1/150°C/0.1M H2SO4/120min			BL Samples [ml]	1800		
Run Characteristics				Total BL [ml]	7660		
Average flow [ml/min]	55.10			Aqueous Rotavap Pot [ml]	2350		
Solid to Liquid Ratio	24.6			Aqueous Rotavap Samp.[ml]	535		
				Total Aqueous [ml]	2885		
Lignin Yield of Run				Cellulose Yield of Run			
Lignin Remains Pot1 [g]	11.23			Feedstock	Pine fine		
Lignin Remains Pot2 [g]	0.65			Mass of Feedstock [g]	400		
Lignin Remains Filter	2.53			MC of Feedstock [%]	9.5		
Lignin Samples [g]	10.32			Dry Mass of Feedstock [g]	365.25		
Lignin BL [g]	36.48			Washed Cellulose [g]	707.26		
MC of Lignin [%]	8.4			MC of Cellulose [%]	345		
Total Lignin Yield [g]	61.21			Dry Mass of Cellulose [g]	158.81		
Total Lignin Yield [%]	17						
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	02:30	200	55	1.34	13%	13%
2	15	02:20	200	65	2.11	20%	33%
3	30	02:10	200	70	2.37	23%	56%
4	45	02:10	200	70	2.07	20%	76%
5	60	02:10	200	70	1.51	15%	91%
6	75	02:40	200	50	0.27	3%	94%
7	90	04:10	200	50	0.25	2%	96%
8	105	04:30	200	55	0.2	2%	98%
9	120	05:00	200	50	0.2	2%	100%

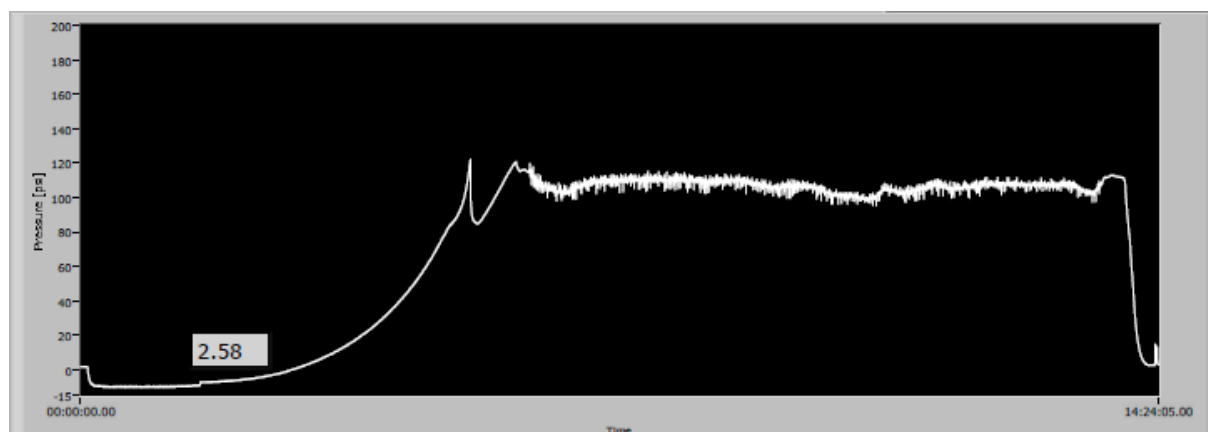


Figure 23. Pressure diagram for run CRC 96.

Table 8. Workup datasheet for run CRC 98.

Run No.	CRC 98			Black Liquor Workup			
Feedstock	400g Pine fine			BL Pot [ml]	7120		
Conditions	-1/130°C/0.1M H2SO4/120min			BL Samples [ml]	1800		
Run Characteristics				Total BL [ml]	8920		
Average flow [ml/min]	56.20			Aqueous Rotavap Pot [ml]	2100		
Solid to Liquid Ratio	25.3			Aqueous Rotavap Samp.[ml]	645		
Lignin Yield of Run				Total Aqueous [ml]	2745		
Lignin Remains Pot1 [g]	1.94			Cellulose Yield of Run			
Lignin Remains Pot2 [g]	0.09			Feedstock	Pine fine		
Lignin Remains Filter	0.28			Mass of Feedstock [g]	400		
Lignin Samples [g]	6.75			MC of Feedstock [%]	9.5		
Lignin BL [g]	30.59			Dry Mass of Feedstock [g]	365.25		
MC of Lignin [%]	8.8			Washed Cellulose [g]	781.28		
Total Lignin Yield [g]	39.65			MC of Cellulose [%]	263		
Total Lignin Yield [%]	11			Dry Mass of Cellulose [g]	215.42		
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	03:40	200	75	0.45	7%	7%
2	15	03:00	200	60	1.12	17%	23%
3	30	02:20	200	75	1.05	16%	39%
4	45	02:30	200	70	0.89	13%	52%
5	60	03:00	200	70	0.89	13%	65%
6	75	03:10	200	70	0.75	11%	76%
7	90	03:10	200	85	0.62	9%	85%
8	105	03:00	200	70	0.52	8%	93%
9	120	03:30	200	70	0.46	7%	100%

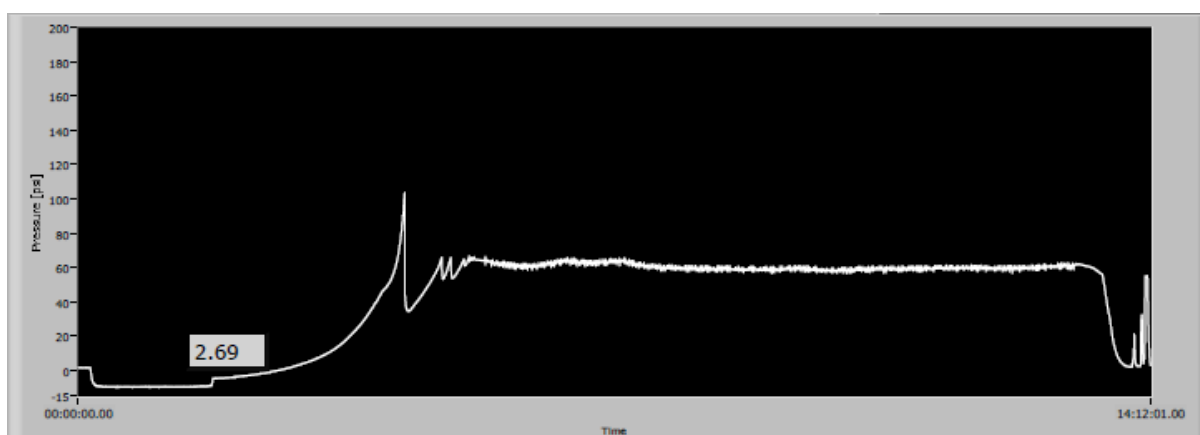


Figure 24. Pressure diagram for run CRC 98.

Table 9. Workup datasheet for run CRC 99.

Run No.	CRC 99		Black Liquor Workup				
Feedstock	400g Eucalyptus fine		BL Pot [ml]	6900			
Conditions	-1/130°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	8700			
Average flow [ml/min]	56.46		Aqueous Rotavap Pot [ml]	2280			
Solid to Liquid Ratio	24.6		Aqueous Rotavap Samp.[ml]	615			
			Total Aqueous [ml]	2895			
Lignin Yield of Run			Cellulose Yield of Run				
Lignin Remains Pot1 [g]	6.5		Feedstock	Eucal. fine			
Lignin Remains Pot2 [g]	0.42		Mass of Feedstock [g]	400			
Lignin Remains Filter	1.07		MC of Feedstock [%]	10.0			
Lignin Samples [g]	16.99		Dry Mass of Feedstock [g]	363.50			
Lignin BL [g]	72.18		Washed Cellulose [g]	809.8			
MC of Lignin [%]	10.3		MC of Cellulose [%]	435			
Total Lignin Yield [g]	97.16		Dry Mass of Cellulose [g]	151.27			
Total Lignin Yield [%]	27						
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	05:00	200	60	0.48	3%	3%
2	15	03:00	200	75	3.77	22%	25%
3	30	03:20	200	75	3.94	23%	48%
4	45	02:40	200	75	3.21	19%	67%
5	60	02:20	200	70	1.85	11%	78%
6	75	02:10	200	70	1.59	9%	87%
7	90	02:30	200	50	1.2	7%	94%
8	105	02:30	200	70	0.68	4%	98%
9	120	03:00	200	70	0.27	2%	100%

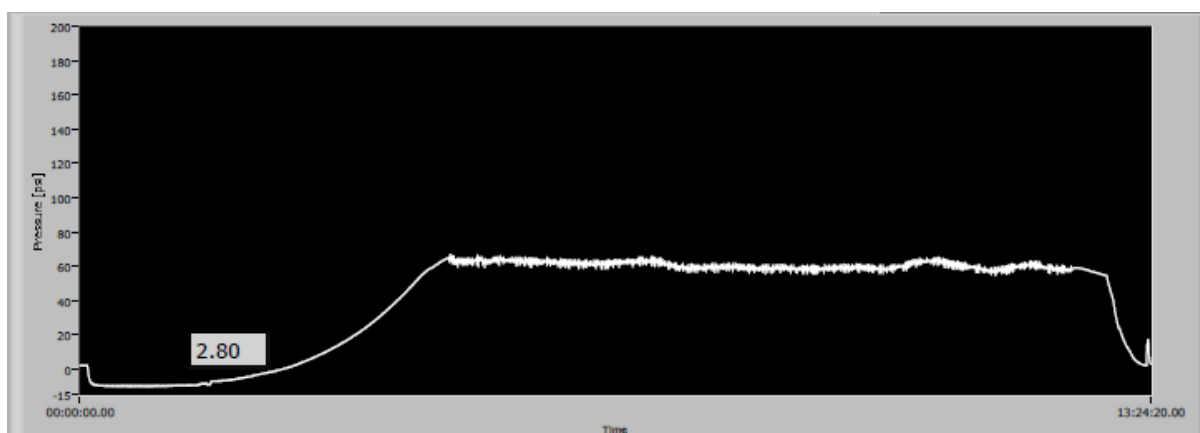


Figure 25. Pressure diagram for run CRC 99.

Table 10. Workup datasheet for run CRC 100.

Run No.	CRC 100		Black Liquor Workup				
Feedstock	400g Eucalyptus fine		BL Pot [ml]	6520			
Conditions	-1/150°C/0.1M H2SO4/120min		BL Samples [ml]	1800			
Run Characteristics			Total BL [ml]	8320			
Average flow [ml/min]	57.27		Aqueous Rotavap Pot [ml]	1890			
Solid to Liquid Ratio	24.5		Aqueous Rotavap Samp.[ml]	755			
Lignin Yield of Run			Total Aqueous [ml]	2645			
Lignin Remains Pot1 [g]	9.2		Cellulose Yield of Run				
Lignin Remains Pot2 [g]	3.06		Feedstock	Eucal. fine			
Lignin Remains Filter	1.85		Mass of Feedstock [g]	400			
Lignin Samples [g]	17.16		MC of Feedstock [%]	10.0			
Lignin BL [g]	68.86		Dry Mass of Feedstock [g]	363.50			
MC of Lignin [%]	7.6		Washed Cellulose [g]	533.29			
Total Lignin Yield [g]	100.13		MC of Cellulose [%]	374			
Total Lignin Yield [%]	28		Dry Mass of Cellulose [g]	112.53			
Lignin Samples							
Sample No.	Run Time [min]	Filling Time [min]	Amount of BL [ml]	Aqueous Phase [ml]	Lignin Yield of Sample	Lignin Yield	Cumulative Lignin Yield
							0%
1	0	03:40	200	75	1.23	7%	7%
2	15	04:20	200	80	4.11	24%	31%
3	30	02:40	200	90	3.5	20%	52%
4	45	03:00	200	75	2.72	16%	67%
5	60	03:00	200	95	1.98	12%	79%
6	75	02:50	200	95	1.43	8%	87%
7	90	03:30	200	95	1.06	6%	93%
8	105	03:00	200	75	0.75	4%	98%
9	120	02:50	200	75	0.38	2%	100%

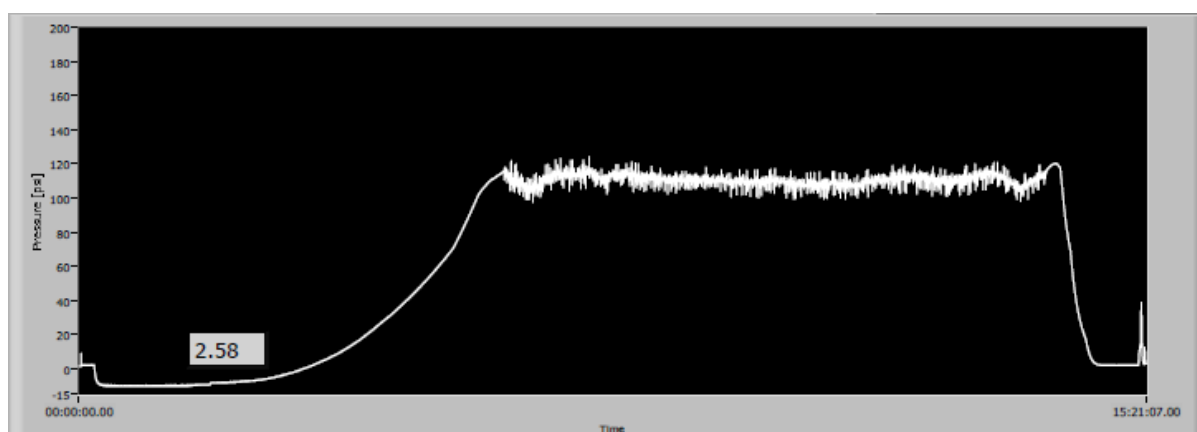


Figure 26. Pressure diagram for run CRC 100.



Figure 27. Samples of black liquor over runtime for run CRC 83.



Figure 28. Samples of black liquor over runtime for run CRC 85.



Figure 29. Samples of black liquor over runtime for run CRC 90.

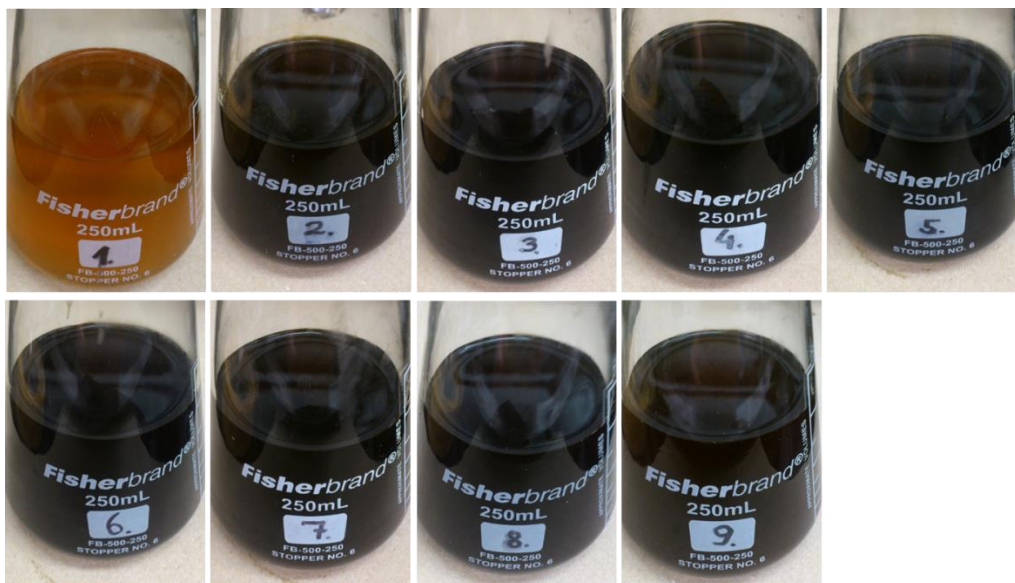


Figure 30. Samples of black liquor over runtime for run CRC 95.



Figure 31. Samples of black liquor over runtime for run CRC 96.



Figure 32. Samples of black liquor over runtime for run CRC 98.



Figure 33. Samples of black liquor over runtime for run CRC 99.



Figure 34. Samples of black liquor over runtime for run CRC 100.

Vita

Thomas Kastenhuber was born March 13, 1994 in Zell am See, Austria. Thomas lived in Saalfelden, Austria, but was raised primarily in Dorfgastein, Austria.

In year 2013, he graduated from Higher Technical College of Business Management focusing on the Timber Industry in Kuchl, Austria. He proceeded to attend college at the Salzburg University of Applied Sciences with concentration in Forest Products Technology and Timber Construction. He designed an undergraduate research thesis evaluating “Study of the Physical and Mechanical Properties of Three-Layer Solid Wood Panels of Modified Poplar”.

During his academic career Thomas gained a lot of international work experience, including a process optimization project at a timber processing company in Tanzania, Africa and a research program at the University of Tennessee, USA.

In September 2015, he began his Masters of Science program in Forest Products Technology and Management under the guidance of Dr. Marius Barbu.