Fachhochschule Salzburg University of Applied Sciences

Designed experimentation for lignin yield from fractionation of cellulose feedstocks

INTERNSHIP AT THE CENTER FOR RENEWABLE CARBON

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Abstract

The interest in converting biomass into chemicals has grown steadily during the last few years, as "our fossil raw materials derived from prehistoric organic matter are irrevocably decreasing." (Biorefineries - Industrial Processes and Products 2005) Nowadays society is rethinking in the development of green products. Energy efficiency is one aspect, but society demands more. It wants products that are sustainable and energy efficient at the same time. To meets society's demands, the United States introduced the 'Energy Independence and Security Act of 2007' as a public law, that among others mandates the production of 21 billion gallons of advanced biofuels[1] by 2022. The superior goal though is to substitute petroleum as the main feedstock for fuel and chemical production by using biomass (e.g. Switchgrass, Poplar). Switchgrass and Poplar provide a solid base to start from, as they are non-food sources and particularly Switchgrass is able to grow in poor soil that cannot support any food crops. To utilize the biomass for the production of fuels and chemicals a pretreatment process that uses the technique of solvent fractionation (an organolsolv process) has been investigated. The lignocellulosic biomass is thereby treated with a ternary solvent mixture and an acid catalyst to isolate cellulose, hemicellulose and lignin.

A series of comparable runs were carried out to see the effects on lignin yield in relation to temperature and acid level. In addition, similar runs were performed to produce as much lignin as possible for further research on the usability of lignin in the production of carbon fibers. To gain more information about the lignin yield over time, an extra run was carried out and 9 samples of black liquor were taken every 15 minutes to show a time curve of the lignin yield.

Key words: biofuels, biomass, organosolv, solvent fractionation, lignin, cellulose, hemicellulose, Switchgrass, poplar, biorefinery

[1] „In general the term ‚advanced biofuels' means renewable fuel, other than ethanol derived from corn starch, that has lifecycle greenhouse gas emissions, [...] that are at least 50 percent less than baseline lifecycle greenhouse gas emissions." House of Representatives of the United States of America 19/12/2007

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1. Introduction

The solvent fractionation process is an organosolv process, as biomass is treated with an organic solvent. The solvent fractionation process requires heat, in order to separate lignin and hemicellulose from lignocellulosic biomass in a delignification process leaving clean, solid phase cellulose that is more accessible to cellulase enzymes for ethanol production (Yang, Wyman 2008). To separate the lignin and hemicellulose fractions the organosolv process breaks their internal bonds. (Pandey 2009) In comparison to more conventional pulping processes, the solvent fractionation process has a number of advantages. (O'Lenick et al. 2009)
These include (Buchinger 2009):

1. The viscosity of the ternary solvent mixture is reduced due to the presence of organic solvents. This improves penetration of the biomass and facilitates a more efficient removal of lignin.
2. The retarding effect of the solvent on the redeposition of lignin onto the fractionated biomass components helps to keep the fractions separated after the separation process is completed. Furthermore is it possible to effectively eliminate the redeposition of lignin through pH control. A more effective lignin removal also diminishes the amount of lignin recondensation and molecular weight increase.
3. Cellulose gained in organosolv processes is easier to purify. This is important in the paper industry i.e.: to consider it as a solution to counteract environmental issues associated with pulp bleaching. Even the chemical industry can benefit from these properties, as it frequently requires starting materials of high purity.
4. The solvent fractionation process is elaborate and recovery of the solvent components can be carried out efficiently.
5. The process offers easy access to all components of the starting biomass feedstock and is economic on small scales.

The Solvent Fractionation process is a Clean Fractionation (CF) process as developed by the National Renewable Energy Laboratory (NREL). The process differs from other organosolv processes as the organic solvent remains in a single phase throughout the entire fractionation process (see Fig. 1).

The CF process treats the feedstock (Switchgrass or poplar) with a ternary mixture of methyl isobutyl ketone (MIBK), ethanol and DI water in the presence of an acid promoter to isolate the cellulose, hemicellulose and lignin. The hemicellulose and the lignin are thereby selec-

tively dissolved by the solvent mixture, whereby the cellulose remains solid to be washed, fiberized and further purified. The soluble fraction that contains the lignin and hemicellulose, also called black liquor, is treated with salt (NaOH) and DI water to induce a phase separation to give an organic and an aqueous phase. The organic phase contains the lignin and the aqueous phase the hemicellulose. The CF process as described can be used for a wide variety of biomass feedstocks (Christensen 2008).

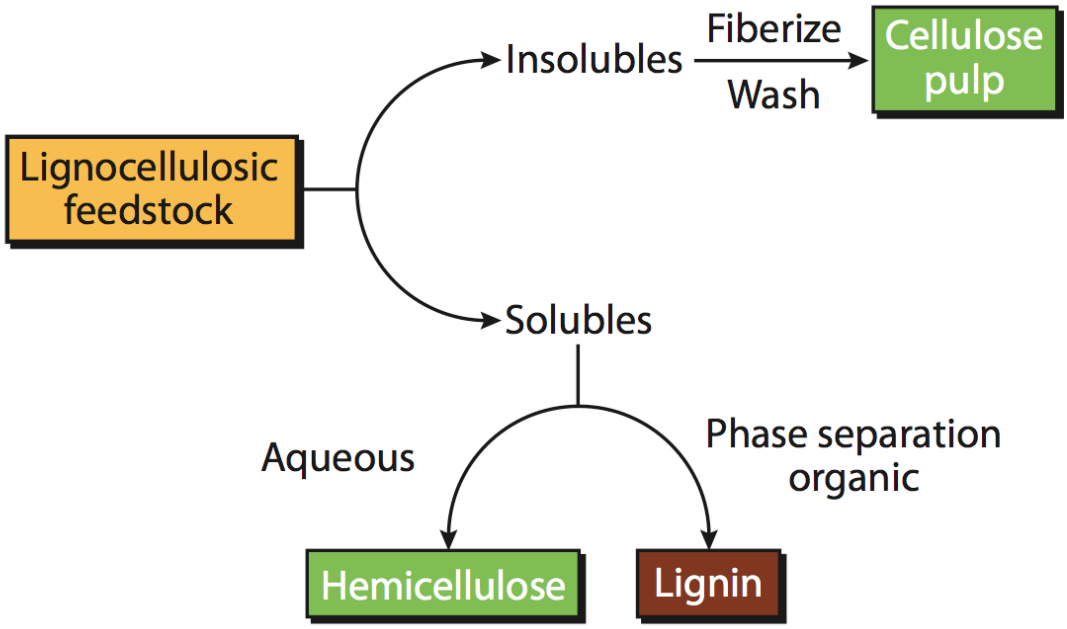

Fig. 1: NREL Clean Fractionation process (Christensen 2008)

2. Material and Methods

2.1. Feedstock

2.1.1. Switchgrass

Switchgrass (Panicum virgatum L.) is a warm-season perennial grass that is native to North America. It is tolerant to poor soils, drought and flooded growing regions. However - to persist several years and produce economical biomass yields it has certain requirements for growth:

- relatively deep soil with a pH level near neutral, which supplies nutrients
- water – either through rainfall or irrigation
- warm climate during growing season (March till July in Oklahoma)

To reach its reproductive stage after dormancy Switchgrass needs at least one month in the north.

The Switchgrass was collected from an established stand of Alamo variety in East Tennessee, air-dried, and comminuted in a 1” knife mill to provide material approximately 1-2” in length.

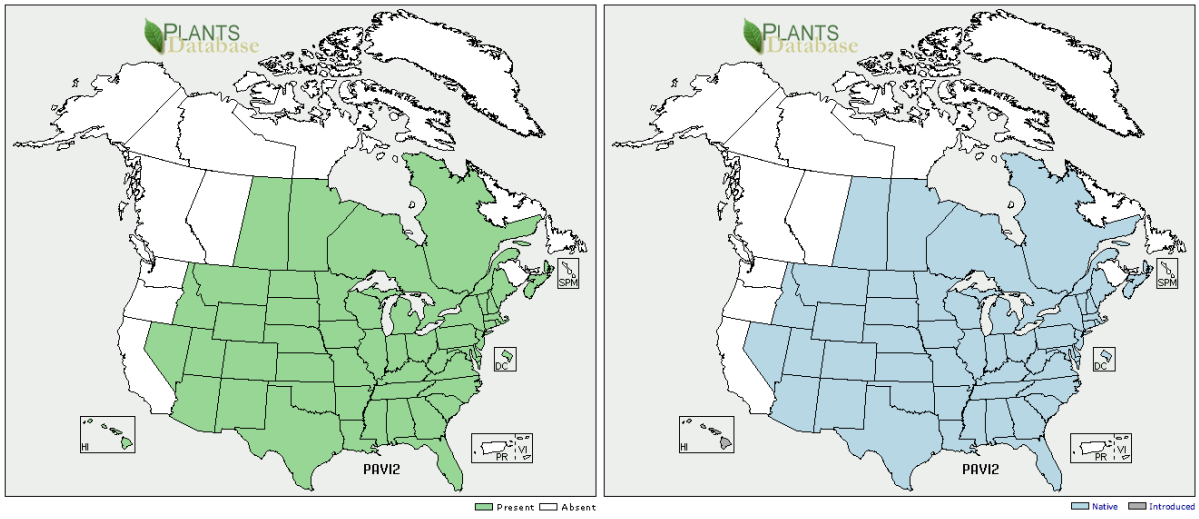

Fig. 2: Switchgrass Distribution on the left and native status on the right side (United States Department of Agriculture 2012a)

2.1.2. White Poplar

White Poplar (Populus alba) is a perennial tree that is native to central and southern Europe, western Siberia and central Asia. The tree was introduced to North America by early settlers and now grows all over North America. It is rapid in growth and thrives in moist areas in re-

gions with hot summers and cold to medium winters. Pulp grade chips produced from White Poplar with dimensions of about 4 cm^2 and thicknesses of 0.5 -1 cm were used in this study.

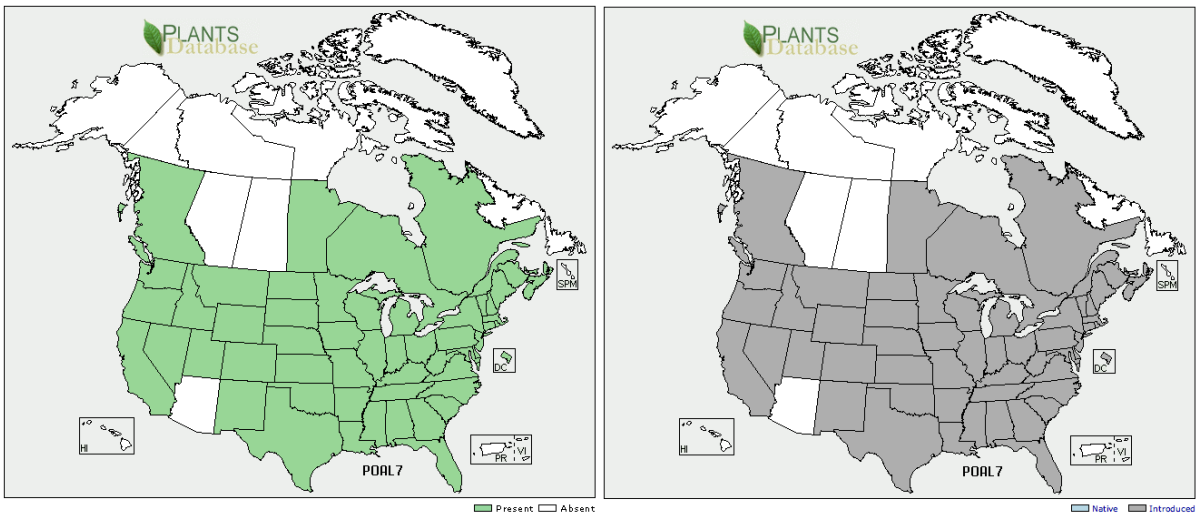

Fig. 3: White Poplar Distribution on the left and native status on the right side (United States Department of Agriculture 2012b)

2.1.3. Solvent

A ternary solvent mixture consisting of methyl isobutyl ketone (MIBK), ethanol and DI water in the presence of an acid promoter, sulfuric acid, was used for the pretreatment of the lignocellulosic biomass.

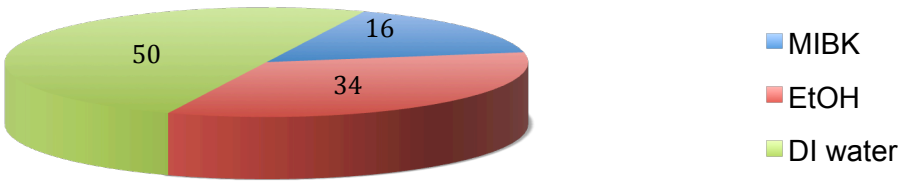

Fig. 4: Ratio of the ternary solvent mixture

2.2. Methods

2.2.1. Fractionation

The Clean Fractionation process, shown in Fig. 5, is divided into 4 phases:

1. Vacuum
2. Filling
3. Heating-Up
4. Feeding

A flow-through Hastelloy reactor is used to carry out the CF. It is charged with a perforated Teflon basket containing the specific feedstock for penetration with an organic solvent. In the

first phase of the CF process a vacuum pump is used to apply a vacuum to the entire system, which leads to a degasification of the feedstock and improves penetration with an organic solvent during the filling stage. The vacuum is applied over a period of 20 minutes and levels off at approximately -11 psi. To trigger the filling of the reactor, the feed tank valve is opened, so that the vacuum fills up the reactor to its outlet at the top. The reactor fills up from bottom to top at a speed of 6 to 10 ml/sec. The filling level is controlled by the amount of solvent that is introduced into a vacuum overflow trap. When 100ml of the solvent appear in the vacuum trap, the valve to the feed tank is closed, the vacuum pump is turned off and the heater bands are turned on to initiate the heating phase. The reactor is equipped with four heater bands that are controlled by electrical PID controllers, which are set at the operation temperature. Usually it takes approximately 45 minutes to heat up the reactor to a core temperature of 140°Celisus. To ensure that the pressure during the heating stage doesn't build up and cause an imbalance inside the reactor, another valve is opened at the time of current pressure eliminates the vacuum. As soon as three of the heater bands reach operation temperature the solvent pump is turned on to allow fresh solvent to be pumped through the feedstock. The pressure that can be reached by the heating process is called equilibrium pressure (P_{eq}).

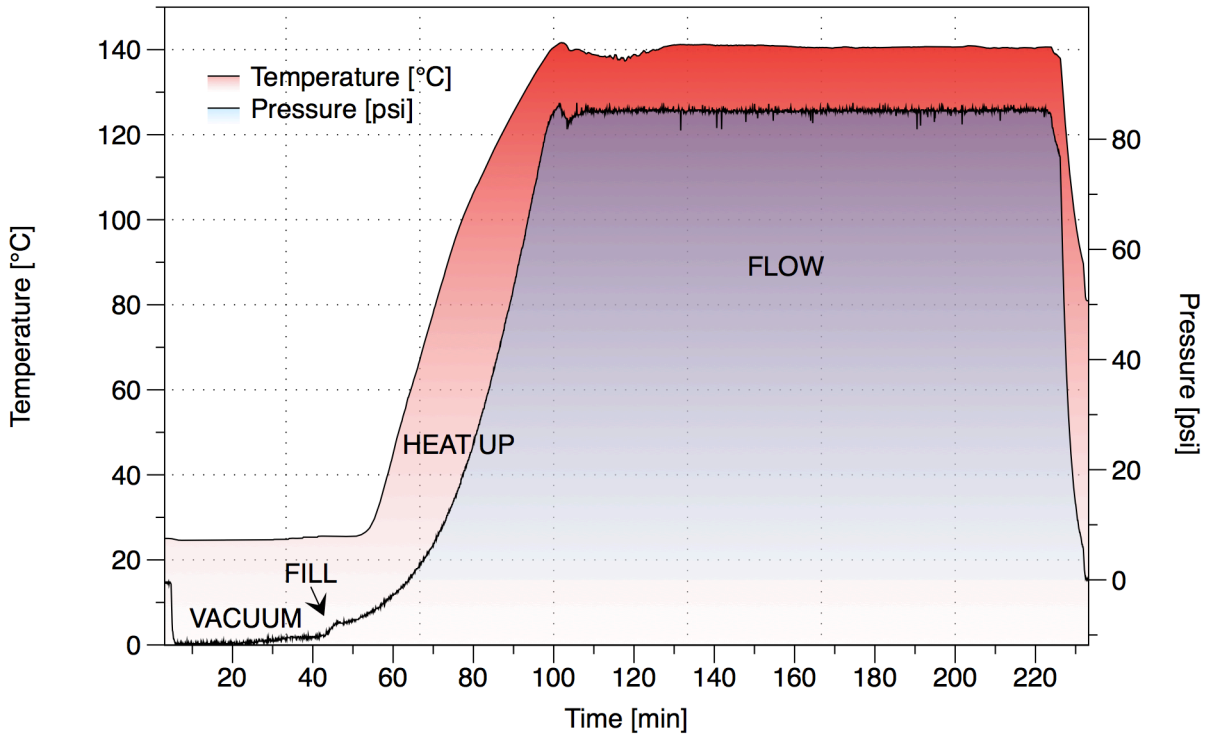

Fig. 5: The 4 phases of the clean fractionation process

After completion of the CF process two phases remain – a solid phase, the cellulose that remains inside the reactor and a liquid phase, called 'black liquor' that contains the hemicellulose and the lignin. The black liquor is continuously collected during the process and after

completion of the run the black liquor that is still inside the reactor is drained into the collection pot too. The cellulose remains inside the reactor until the reactor is cool enough to open and to remove the perforated Teflon basket with the cellulose inside.

2.2.2. Processing

2.2.2.1. Black Liquor

As the black liquor contains both – hemicellulose and lignin – the next step is the separation of these two components. Before the actual separation is carried out the black liquor is filtered with a fast-flow filter paper using a Buchner funnel to remove solid biomass components (e.g. Cellulose) that have come through the reactor pipes. To induce the separation of these two components NaCl is added, the mixture is then shaken and the layers allowed to separate for at least 30min (see Fig. 6). During this time the NaCl connects with the deionized water that is part of the organic solvent, which leads to the phase separation.

$$Volume\ [ml] \cdot 0{,}5 \cdot 0{,}15 = NaCl\ [g]$$

Volume [ml]: volume of black liqour

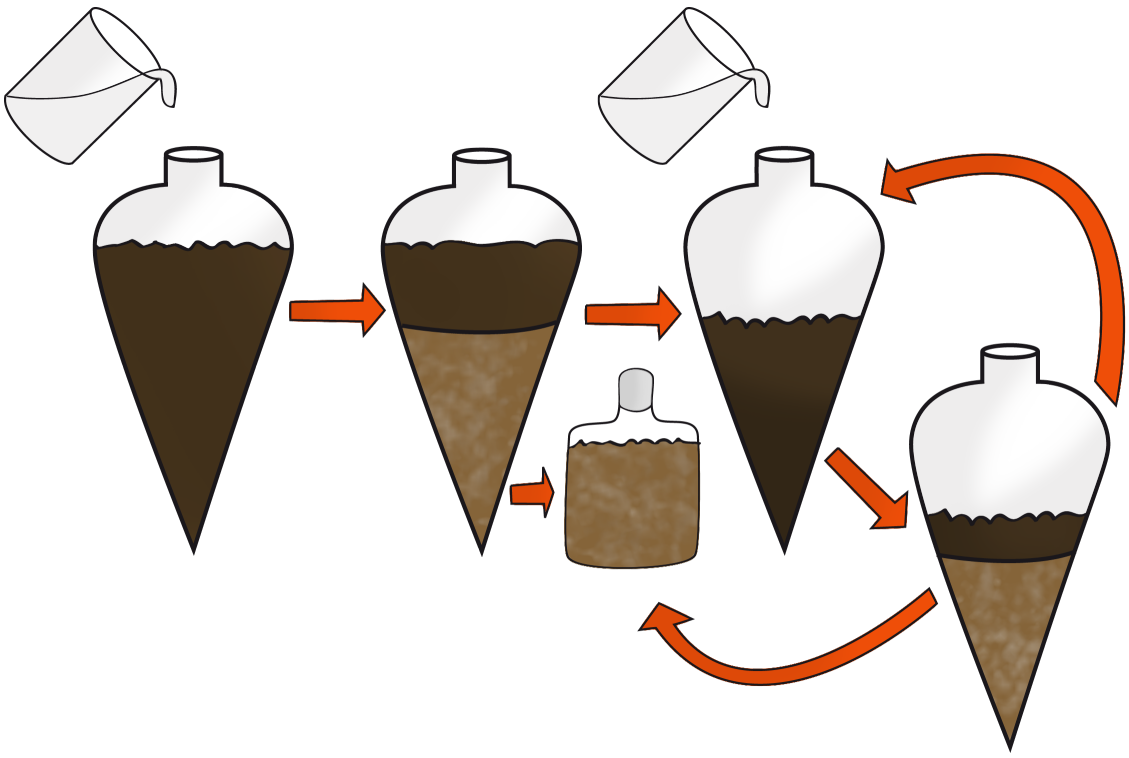

Fig. 6: Process operation for black liquor separation

The organic layer containing lignin is at the top and the aqueous layer with the hemicellulose at the bottom of the separation funnel. The layers are then separated and the organic layer is washed with additional deionized water to remove residual EtOH and sugars contained in the solvent. This step is repeated once, whereby the time for the separation of the layers shortens.

$$Volume\ [ml] \cdot 0{,}3 = DI\ water\ [ml]$$

Volume [ml]: volume of organic layer

2.2.2.2. Hemicellulose isolation

A rotary evaporator is used to remove the EtOH from the aqueous phase that is collected during the separation of the black liqour. As the aqueous phase still contains lignin the remaining liquid is filtered with a medium-flow filter paper using a Buchner funnel to remove this so-called aqueous lignin. For further analysis of the Hemicellulose a 100ml sample of the filtrate is stored in a freezer. The aqueous lignin gained is dried under high vacuum, weighed and stored for further processing.

2.2.2.3. Lignin isolation

For lignin recovery the organic layer is mixed with the dried aqueous lignin and concentrated with a rotary evaporator at 50°C to obtain a dry gummy clay-like material. This material is then treated with diethyl ether (Et_2O) to result in lignin powder. For better treatment, it is scratched off the surface and reduced to small pieces to make it more accessible for the Et_2O. The Et_2O is then filtered off and the lignin is dried by vacuum for approximately 15min. The treatment with Et_2O is repeated 3 to 4 times until the lignin is powdery. When this is accomplished the lignin is dried overnight under vacuum, conditions, weighed and stored afterwards.

2.2.2.4. Cellulose

After unloading the reactor the cellulose is mixed with 3 liters of deionized water and kept over night to ease fiberization. A blender is used to fiberize the cellulose for a better removal of the solvent that was used during the fractionation process and as a preparation for further downstream processing. The cellulose is then placed in a Buchner funnel, using vacuum to pull deionized water through the cellulose as a cleansing process (see Fig. 7). Covering the funnel with a latex membrane after one hour of washing causes the vacuum to compress the

cellulose and removes the water. This is done for about two hours and the cellulose is then weighed and stored in a freezer for further processing.

Fig. 7: Schematic view of the cellulose washing.

2.2.3. Klason-Lignin and Ash

A Klason lignin determination is performed to gain an insight of how much insoluble lignin is inside the produced lignin, cellulose and the starting feedstock (Switchgrass and Poplar). As the lignin is obtained in powdery form, there is no need to grind it. The cellulose and the starting feedstock – however – are ground first, using a Wiley mill (mesh size 40). At first the moisture content is determined by placing 2 - 3g of the air-dry material in a 105°C oven overnight.

$$\frac{(wt.of\ pan + wet\ biomass) - (wt.of\ pan + dry\ biomass)}{(wt.of\ pan + dry\ biomass) - wt.of\ pan} = \%\ moisture\ content$$

Duplicate samples of 300mg of the oven-dried material are then placed in pressure bottles and 3ml of 72% H_2SO_4 are added, one at a time using an Eppendorf pipet. For better penetration, each sample is stirred for 1 minute and then placed in a 30°C water bath, where it remains for another one and a half hours and is stirred every 15 to 20 minutes. Immediately afterwards the solution is diluted to a concentration level of 2.4% H_2SO_4 using 84ml of DI water and stored in an autoclave at 120°C for two and a half to three hours. The samples are filtered afterwards using filtering crucibles that were dried in a 105°C oven overnight and those crucibles with the residue (Klason lignin) are then again placed in a 105°C oven overnight to measure the oven-dry-weight of the residue and to calculate the amount of Klason lignin.

$$\frac{(wt.of\ crucible + residue) - wt.of\ crucible}{wt.of\ biomass} = \%\ Klason\ lignin$$

A sample of the filtrate is kept for each sample for further analysis concerning the content of soluble lignin, which is not considered within the framework of this project.

Furthermore the crucibles with the residue are placed in a muffle oven at 575°C overnight to determine the ash-content of the Klason lignin samples. Before measuring the weight of the samples the muffle oven is turned down to 175°C and first opened when stable at 175°C. The crucibles are then placed in a desiccator for 30 minutes to cool down before measuring.

$$\frac{(wt.of\ crucible + ash) - wt.of\ crucible}{wt.of\ biomass} = \%\ ash$$

3. Reactor

The reactor used at the Center for Renewable Carbon is designed and used as a flow-through reactor. Since the reactor constantly comes in contact with strong chemicals (e.g. sulfuric acid) it is made from Hastelloy® C-276 alloy. „Hastelloy® C-276 alloy is a nickel-molybdenum-chromium wrought alloy that is generally considered a versatile corrosion resistant alloy.“ (Haynes International 2001) C-276 alloy has excellent resistance properties against a wide variety of chemicals such as hot contaminated media (organic and inorganic), chlorine, formic and acetic acids (Haynes International 2001).

To degasify the feedstock and thereby improve the penetration with the organic solvent, the reactor is equipped with a vacuum pump (DOA-P707-AA from GAST) in order to to apply a vacuum on the entire system. Furthermore four heater bands from Watlow® are installed to heat the reactor to operation temperature. The heater bands are controlled by electrical PID/On-Off Controllers (CN9000A) from Omega® that are set to operation temperature and measure the actual core temperature of the reactor through Dual Element Thermocouples. When operation temperature is reached the solvent is pushed through the reactor using a Williams Chemical Injection Pump (CR P500V225) that uses an Oscillamatic® Controller to control the stroke rate (see Fig. 8). The stroke rate depends on the supplied air pressure and is therefore an unscaled factor from 0 – 100. It is manually adjustable at the top of the Oscillamatic® Controller just by turning the Stroke Rate Control Knob.

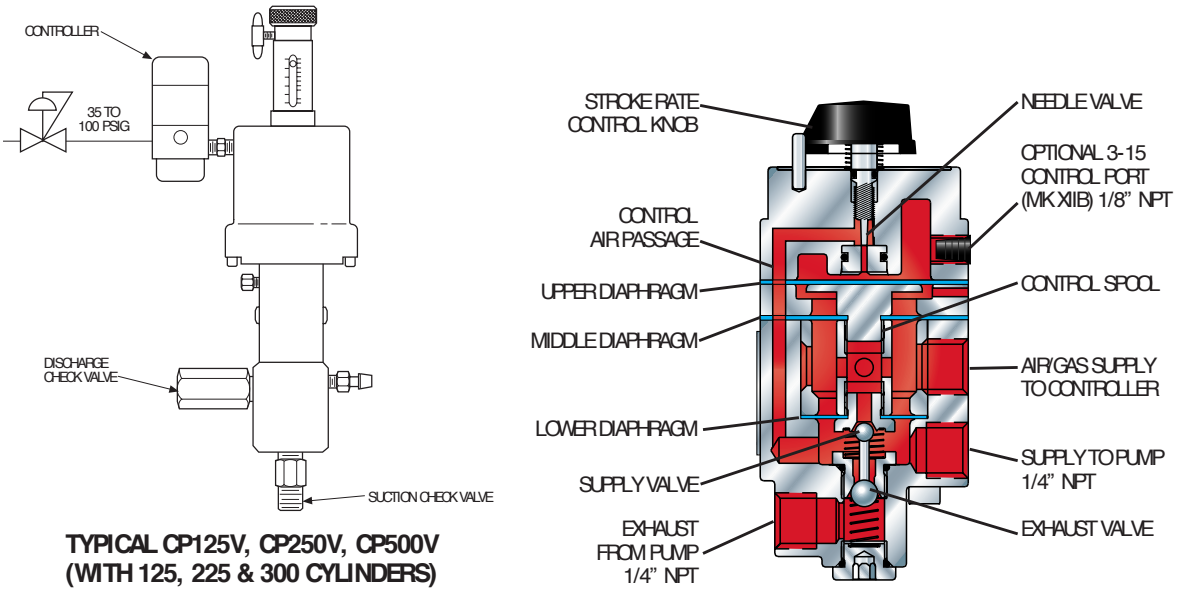

Fig. 8: Williams pump and its Oscillamatic® Controller (WILLIAMS Instrument Incorporated Milton Roy 1999)

The maximum volume per stroke is specific for the pump (3.2 ccm) and can be reduced manually. (WILLIAMS Instrument Incorporated Milton Roy 1999) This parameter is called Stroke Length – it is an adjustment directly at the pump. The default setting for the reactor is 1.5 ccm stroke volume and a stroke rate of 10. Despite all of these custom settings, the actual flow is controlled by a badger valve (766 BLRA Model 4), whereby an ITT Conoflow (Model GT4108) controls the valve by converting an input signal of 4-20 mA DC to a proportional 3-27 PSIG output (Buchinger 2009). The signal is generated by an analog Input/Output Module (NI cFP-AIO-600) that is mounted to an Ethernet/Serial Interface (NI cFP1808) and receives commands via NI Compact FieldPoint from a VI (virtual instrument) in LabView.

„LabVIEW is system design software that provides engineers and scientists with the tools needed to create and deploy measurement and control systems through unprecedented hardware integration.“ (National Instruments 2012b) It is an intuitive graphical programming environment using the dataflow language G that makes programming a lot easier (see Fig. 9). “G programming is performed by wiring together graphical icons on a diagram, which is then compiled directly to machine code so the computer processors can execute it.“ (National Instruments 2012a)

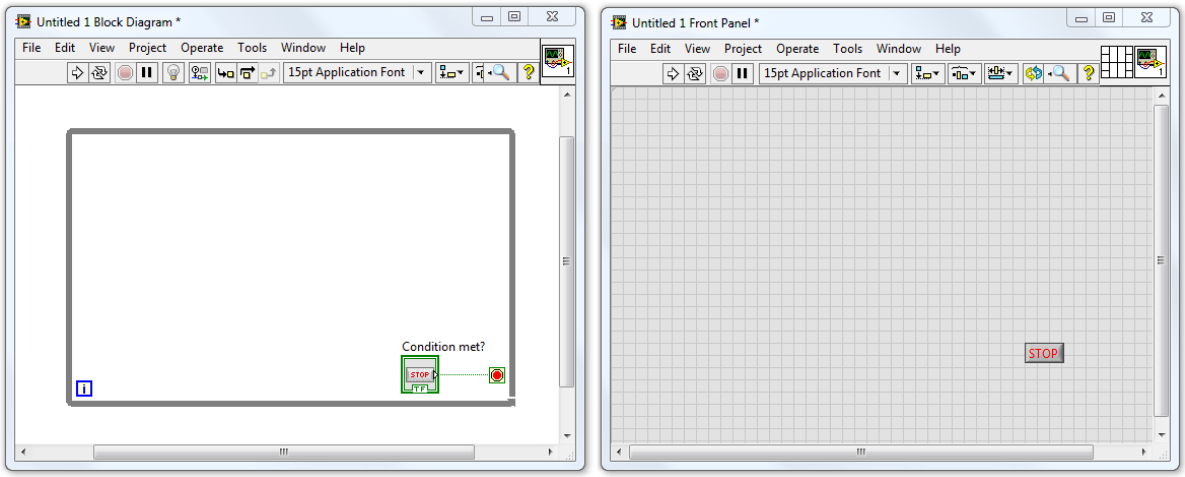

Fig. 9: A While Loop in G is intuitively represented by a graphical loop, which executes until a stop condition is met. (National Instruments 2012a)

Programs and subroutines in LabView are called virtual instruments (VIs) and consist of three components: a block diagram (programming environment), a front panel (user interface) and a connector panel that is used to represent the VI in the block diagrams of other, calling VIs.

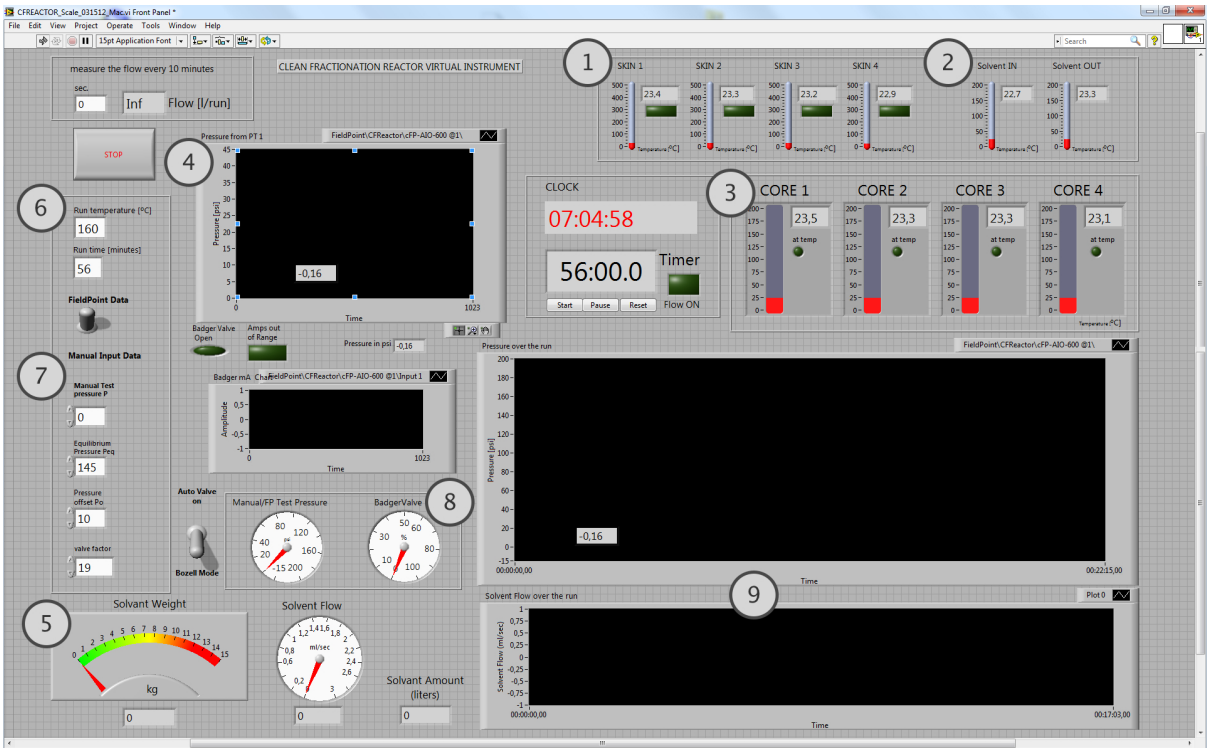

Fig. 10: VI for measurement data acquisition, data evaluation and direct control of the pressure inside the reactor

The VI that is shown in Fig. 10 represents the control unit that is used for the reactor. Sudden failure of the LabView Software will not cause any safety issues, as there are several conventional measuring instruments and a safety valve to control pressure and temperature of

the reactor in such situations. The range of functions of the VI includes measurement data acquisition, data evaluation and direct control of the pressure inside the reactor through the automation of the badger valve opening.

Setup of the control unit (VI) shown in Fig. 10:

1. Display of the current skin temperature [°C] of the reactor. There are 4 indicators as the reactor has 4 Thermocouples implemented. “SKIN 1” at the top to “SKIN 4” at the bottom of the reactor. The VI has a function implemented to alert the operator visually and acoustically when the skin temperature reaches 400 °C. The measured data is written to a log file.

2. Display of the current solvent temperature [°C]. There are 2 indicators implemented to show the solvent temperature before entering “Solvent IN” the reactor and after coming out “Solvent OUT” of the reactor. The measured data is written to a log file.

3. Display of the current core temperature [°C] of the reactor. There are 4 indicators as the reactor has 4 Thermocouples implemented. “CORE 1” at the top to “CORE 4” at the bottom of the reactor. The measured data is written to a log file.

4. Display of the current pressure [psi] inside the reactor and the past 1022 readings of the pressure transducer (PX319-300GI). The readout of this pressure transducer is very important, as it might be a safety issue during the run. But the value is also integrated in some calculations and has an effect on the opening of the badger valve. The measured date is written to a log file.

5. Display of the actual weight of the solvent and automatic calculation of its flow [ml/sec] and volume [liters]. The continuous measured data from the scale and the results from both calculations are written to the log file that is created while the VI is running.

$$\frac{Solvent\ [kg]}{1{,}111} = Solvent\ [liters]$$

6. Manual data input of the run temperature [°C] and run time [mins]. Whereby the run temperature is only used to indicate whether the core temperature has already reached the set run temperature. Yet the temperature is still controlled via electrical PID/On-Off Controllers as described before. The run time is only used as a value for

the electronic time clock. Both variables (run time and run temperature) are not yet written to the log file that is created while the VI is running.

7. Manual data input of the equilibrium pressure [psi], pressure offset [psi] and the valve factor [%]. These manually set values and the current value from the pressure transducer are used to directly control the opening of the badger valve. These values run through several functions, shown in Fig. 11, and result in a value that is sent to the analog input of the badger valve.

```
if (currentPressure [psi] ≥ (offsetPressure [psi] + equilibriumPressure [psi]) {

    x = (4,444E-4 * currentPressure [psi]) * (valveFactor / 100);

}

else (currentPressure [psi] < (offsetPressure [psi] + equilibriumPressure [psi]) {

    x = 0;

}


if (x < 0,02) {

    y = x;
    writeValue (y) to BadgerValveInput;

}

else (x ≥ 0,02) {

    y = 0,02;
    writeValue (y) to BadgerValveInput;

}
```

Fig. 11: Illustration of the functions used to control the opening of the badger valve

For testing purposes of the VI it is possible to switch between FieldPoint Data (data provided by the sensors) and Manual Input Data. However, this has so far only been implemented for the pressure transducer.

8. Indicates the opening of the badger valve [%]. According to Rene Buchinger (Buchinger 2009) this value should be around 60% to reduce fluctuations of the pressure inside the reactor.

9. Indicators of the pressure and the flow rate history over the complete run.

4. Results and Discussion

Fractionation of Poplar, Switchgrass and Lignin isolation. “To approximate operation conditions in a commercial biorefinery, the feedstock was only minimal prepared prior to fractionation. Samples of Alamo Switchgrass were air-dried and chopped into 1-2” length, however, extractives were not removed nor were plant anatomical fractions separated.” (Bozell et al. 2011) Samples of White Poplar were air-dried and cut into pulp grade chips with dimensions of about 4 cm^2 and thicknesses of 0.5 -1 cm. A determination of the moisture content of the starting material revealed an average moisture content of 8.94% for Poplar and 8.33% for Switchgrass. The fractionation process was carried out in a flow-trough Hastelloy pressure reactor at temperatures of 140 and 160 °C, using a single-phase ternary mixture of methyl isobutyl ketone, ethanol and DI water in the presence of a sulfuric acid catalyst at concentrations of 0.05 and 0.1 M.

4.1. Lignin yield

Tab. 1: Summary of Individual Switchgrass and Poplar Fractionation Runs and Lignin Yields (run time 2h)

run no.	feedstock	H_2SO_4 [M]	temperature [°C]	lignin yield [a] [g]	lignin yield [a,b] [%]	lignin yield [c] [%]
172	poplar	0.05	160	131.22	18.32	79.24
171	switchgrass	0.05	160	64.1	14.91	89.26
174	poplar	0.1	140	124.32	17.27	75.07
175	switchgrass	0.1	140	69	16.05	96.09
176	poplar	0.1	160	130.52	18.13	78.82
177	switchgrass	0.1	160	62.94	14.64	87.65
180	poplar	0.05	140	111.94	15.55	67.60
178	switchgrass	0.05	140	68.64	15.96	95.59

[a] Total yield of lignin after washing with ethyl ether and DI water. [b] Refers to the mass of the starting feedstock. [c] Yield based on lignin in feedstock referring to literature.

Tab. 1 shows all individual Switchgrass and Poplar fractionation runs that were carried out in this study. The results indicate that Switchgrass has over-all a better lignin yield than Poplar. On average Switchgrass reaches a lignin yield of 92.15% (15.39% referring to the mass of the starting feedstock) and Poplar 75.18% (17.32%) according to indications in literature. It is interesting that both Switchgrass and Poplar react in the same way to a change in the acid level. For both the lignin yield decreases at a run temperature of 160 °C, when the acid level

is changed from 0.05 to 0.1 M. However, there is hardly any change in the results. At a run temperature of 140 °C it decreases when the acid level is changed from 0.1 to 0.05 M. For Switchgrass there is still hardly any change in the results but for Poplar the change is intensified. Furthermore it is interesting that the lignin yield for Switchgrass decreases, when run temperature is changed from 140 to 160 °C and does not increase as it does with Poplar.

4.2. Lignin yield over time

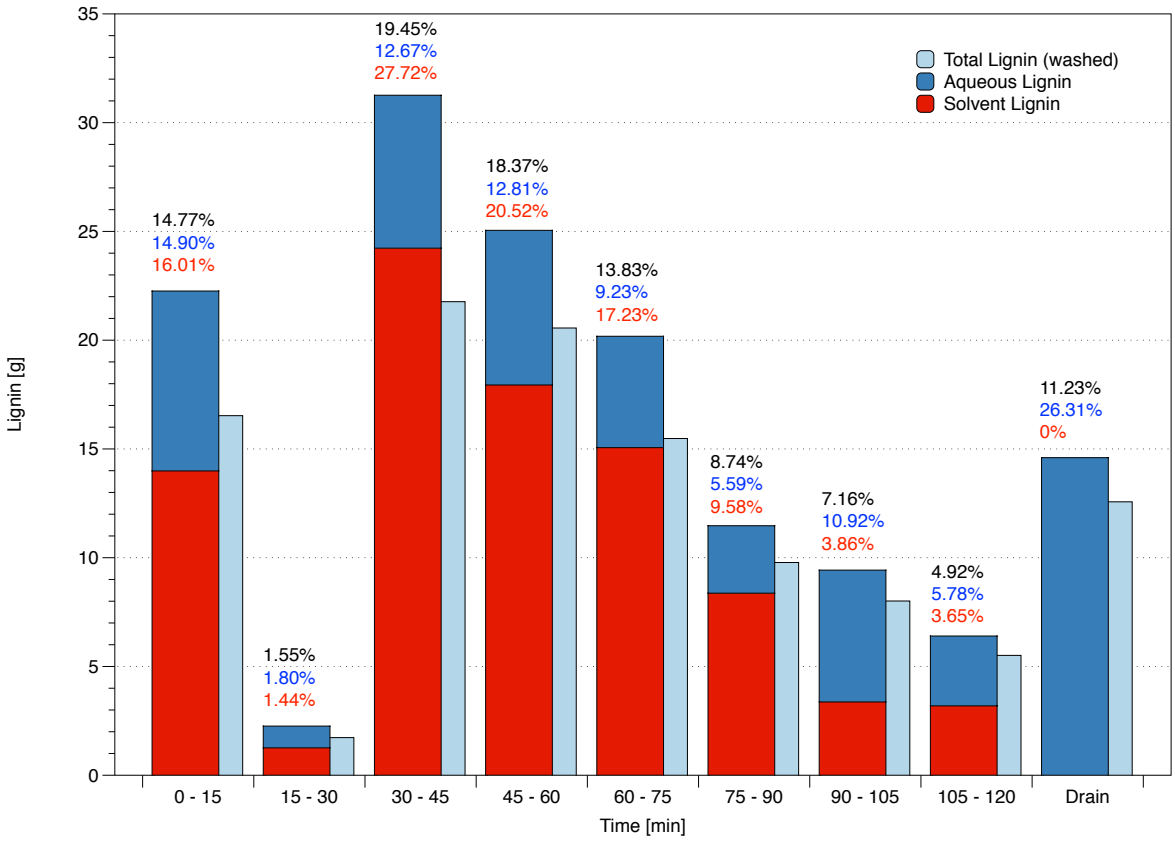

Fig. 12: Lignin yield over time for Poplar fractionation run # 180 (140°C / 0.05 M /2h). Percentages refer to the mass of the starting feedstock.

The determination of lignin yield in relation to time is a crucial point for the optimization of the Clean Fractionation process, as it provides detailed information about how much lignin is removed in a specific period of time. Fig. 12 shows the first attempt to determine the lignin yield for a Poplar fractionation run at 140 °C using 0.05 M H_2SO_4.

To determine the lignin yield over time, every 15 minutes the collecting pot for the continuous outflow of the black liquor was changed. Every pot was filled with an additional 500ml of fresh organic solvent to prevent the black liquor from sticking to the surface of the pot. The last sample that was taken from the run contained all black liquor that was drained from the

reactor after shutdown. Each sample was handled separately through the whole process of the separation and isolation of the lignin.

For more information about the process, see chapter 2.2 Methods.

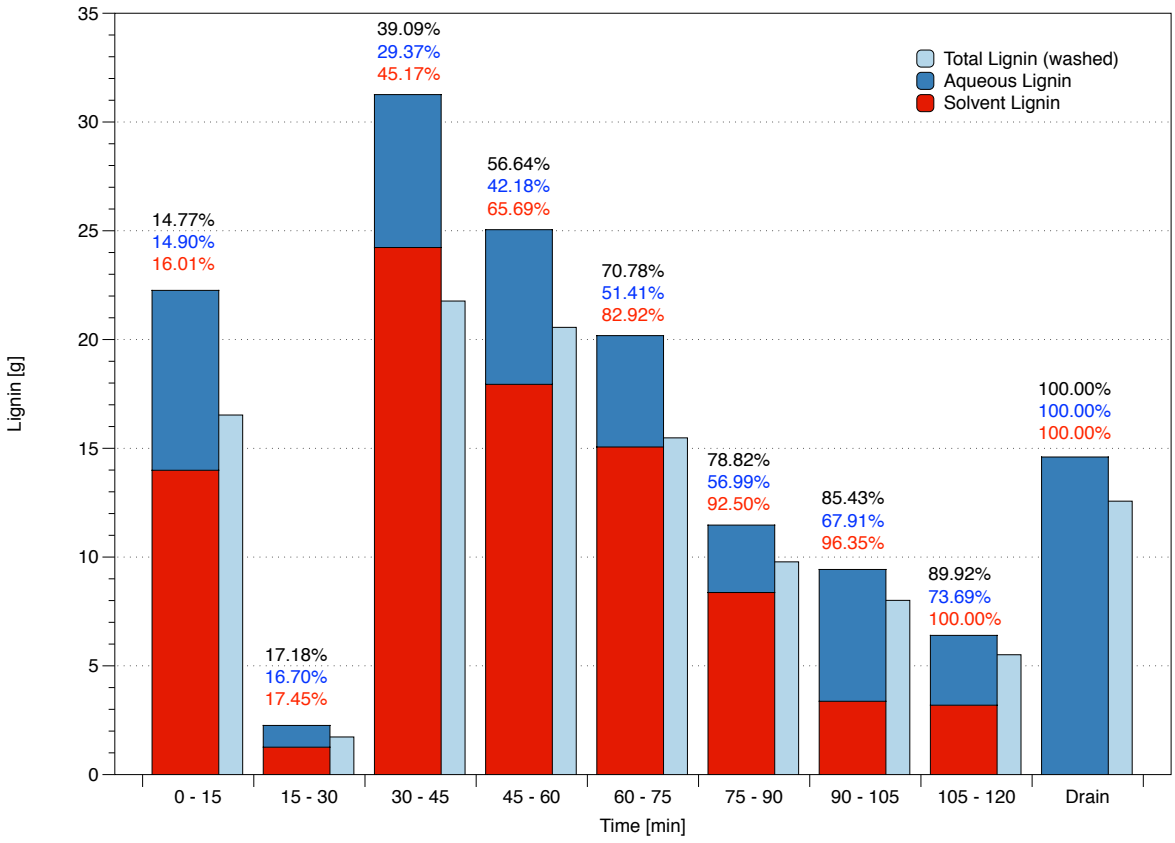

Fig. 13: Lignin yield over time for poplar fractionation run # 180 (140°C / 0.05 M /2h).

As shown in Fig. 12 and Fig. 13 the distribution of the lignin yield peaks after 45 minutes and reaches a yield of nearly 40% of the total, washed lignin. Obviously the second sample varied tremendously from the trend of the distribution. This might be a consequence of a clogged reactor outlet during this time or a failure during further processing of the black liquor. It is advisable to schedule a series of identical runs to see whether this result is repeatable or unprecedented.

If it should emerge that this distribution, except that for the second sample, is more or less highly diagnostic, the next step would be to check how the different temperature conditions and the H_2SO_4 concentration have an effect on this distribution. The goal would be to remove as much lignin as possible in a shorter period of time. But if the approach is too aggressive this might result in poor quality lignin. This problem has to be considered as well in further investigations.

4.3. Klason-Lignin

Tab. 2: Klason Lignin Analysis on lignin Samples with different run conditions

run no.	lignin	feedstock [POP/SG]	H_2SO_4 [M]	temperature [°C]	run time [mins]	klason lignin [%]
129	OR	50/50	0.05	120	56	103.18
						87.43
131	OR	50/50	0.025	140	56	85.68
						85.88
133	AQ	90/10	0.1	140	56	84.55
						84.47
137	AQ	90/10	0.025	120	56	58.17
						75.16
158	AQ	10/90	0.05	160	90	81.10
						82.39
159	AQ	90/10	0.1	160	90	89.13
						88.07
165	AQ	10/90	0.05	140	56	82.21
						83.04
165	OR	10/90	0.05	140	56	86.37
						86.16
161	OR	90/10	0.025	120	56	85.81
						85.74

The red numbers indicate mistakes.

Lignin is very complex organic polymer that is found in the cell walls of plants where it binds with the cellulose creating strong, robust cell walls. Due to its structure, it could play a central role as a chemical feedstock but it is not easy to determine the purity of the lignin. There are several methods (e.g. the permanganate method & the acetyl bromide method) for the determination of lignin, however, the Klason lignin method was the one selected for this study. The Klason lignin defines lignin as insoluble in 72% sulfuric acid. As some lignin may be lost during the hydrolysis with H_2SO_4, the filtrate has to be checked for soluble lignin as well. The analysis of the soluble lignin was not part of this study. The results that are shown in Tab. 2 indicate an average percentage of 85.94% Klason lignin for the produced organic lignin and 84.37% Klason lignin for the aqueous lignin. The higher the percentage of Klason lignin, the purer the lignin as given in the Klason lignin definition.

Tab. 3: Klason Lignin Analysis on fractionated cellulose samples with different run conditions

run no.	feedstock [POP/SG]	H_2SO_4 [M]	temperature [°C]	run time [mins]	klason lignin [%]
129	50/50	0.05	120	56	28.59
					16.37
131	50/50	0.025	140	56	10.89
					10.24
133	90/10	0.1	140	56	4.89
					5.14
137	90/10	0.025	120	56	20.84
					28.10
153	50/50	0.1	120	90	10.73
					15.26
156	10/90	0.1	140	90	6.61
					6.45
158	10/90	0.05	160	90	5.86
					5.93
159	90/10	0.1	160	90	2.42
					2.87
161	90/10	0.025	120	56	19.37
					18.70
163	90/10	0.05	120	90	17.46
					17.82
165	10/90	0.05	140	56	8.88
					7.83
170	0/100	0.05	140	90	7.91
					7.94

The red numbers indicate mistakes.

The Klason lignin analysis on fractionated cellulose samples was carried out to show how well the CF process works. The lower the percentage of the Klason lignin, the better the separation of the lignin and the cellulose. Run number 159 indicated a very good separation of the two components.

5. Suggestion

5.1. Reactor

To simplify the workflow at the reactor it is worth considering relocating some of the valves, to make them more accessible for the operator. One place for all valves would be even better, especially for time-critical adjustments to the fractionation process. Furthermore it would be useful to implement a purging pipe, so that it is no longer necessary to disassemble several reactor pipes.
Using a different reactor lid could accelerate the production of larger quantities of lignin. At the moment it is necessary to wait until the components are cool enough to open the reactor lid. As this takes around 45 minutes, depending on the run temperature, it is worth considering a clamping fastener.

5.2. LabView

The VI that is used to control the reactor is already quite good, but there are some functions that are improvable. So far the VI is used primarily to collect data from the sensors and visualize them through indicators and diagrams. That works quite well, but the way in which this data is presented on the screen and stored in the log file could be optimized. The VI runs in a continuous loop to readout the sensors. For some good reasons the specified time [seconds] to delay running the calling VI is set to 0.05 seconds. This is not a problem but apparently it was not considered during the implementation of the history diagrams (#4 and #9 shown in Fig. 10). Because of the 0.05 second delay the time shown in these history diagrams flies by 20 times faster. For the interpretation of these diagrams, it may be worthwhile to convert the time axis into the actual time that has passed (hh:mm:ss).
Furthermore it would be worth the effort to implement a database to store all measurements by the sensors and all the manual inputs by the operator. This would reduce the administration expense for data preparation and especially prevent data loss in mountains of paper. Everything would be stored in one place and accessible from every workstation. Applications like FileMaker could access the database for automated preparation of standardized diagrams. All log files of the VI used so far do not have the specific run number, the chosen run temperature and the acid level of the solvent stored inside the file. If someone is looking for past runs with specific run conditions it is extremely time-consuming to find all data that belong to them.

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Figures

Tables

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