

INTERNSHIP AT THE FOREST PRODUCTS CENTER

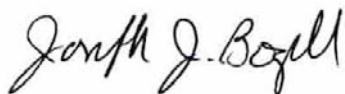
Solvent fractionation process for switchgrass

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1 Symbols and Abbreviations

1.1 Mathematical Symbols

n	number of samples
s	standard deviation
r	Pearson correlation coefficient
r^2	coefficient of determination
\bar{x}	mean
τ	Kendall Tau correlation
min	minimum
max	maximum

1.2 Chemicals

MIBK	methyl isobutyl ketone
DI H ₂ O	distilled water
EtOH	ethanol 180 proof

1.3 Abbreviations

AQ	aqueous
CF	clean fractionation
P_{eq}	equilibrium pressure
PT	pressure transducer
VI	virtual instrument
i	increment
PID	proportional incremental derivative controller

1.4 Tradenames

SPSS	SPSS, Inc.
Excel	Microsoft Corporation
JMP	SAS Institute Corp.
SigmaPlot	Systat Software Corp.
MAX	measurement and automation system
LabVIEW	National Instruments Corp.

2 Abstract

Interest in recovering cellulose from biomass has grown steadily over the last few years as cellulose can be enzymatically hydrolyzed to sugars and fermented to ethanol. Under the Energy Independence and Security Act of 2007, refiners must produce 21 billion gallons of non-cornstarch products by the year 2022. Switchgrass is a very promising lignocellulosic source for this ethanol. Switchgrass is a versatile and adaptable plant, as it can grow in different weather conditions. It is a perennial and can grow in poor soils that cannot support any food crops. It is not a food source so it will not compete for food crops. To isolate the required cellulose from switchgrass, the technique of solvent fractionation, an organosolv type of process, has been investigated. Solvent fractionation is a process of choice for pretreatment because the process is suitable for use with several different biomass feedstocks, as it gives favorable separations. With the correct parameters, it is easy to isolate products after fractionation, and along with that, offers recovery of each component in a high yield and purity amenable to conversion to other chemicals.

Fractionation technology developed at the National Renewable Energy Laboratory (Clean Fractionation) is being implemented at the University of Tennessee for the separation of switchgrass into its primary components. The fractionation uses a mixture of organic solvents and water to separate switchgrass into cellulose, lignin and hemicellulose for the production of fuels and chemicals. To operate the fractionation reactor, biomass and a ternary solvent mixture, with sulfuric acid catalyst, are added to a 3.5 L, 3" bore, pressurized, Hastelloy flow-through reactor, controlled via LabVIEW and operating at three temperatures: 120 deg C, 140 deg C, and 160 deg C. After the reaction is complete in 56 minutes, the products of the reaction are in a solid phase, organic phase, and aqueous phase. The solid phase, primarily cellulose, is filtered and washed free of the reaction. The aqueous phase, containing hemicellulose, sugars, and catalyst, is obtained from a separatory funnel that separates this aqueous phase from an organic phase. The organic phase is then further processed to obtain organic soluble lignin, which is suitable for additional applications. 2D NMR and FTIR has been used on our lignin to obtain qualitative spectra for comparison and these will be presented.

3 Solvent Fractionation Process

In general the Solvent Fractionation Process is an organosolv process. The Organosolv process is a delignification process with organic solvents using a mineral acid as catalyst. This method breaks the internal lignin and hemicellulose bonds and separates the lignin and hemicellulose fractions that can be potentially converted to useful products (Pandey 2009). This process works well on hardwood, corn and switchgrass (*Panicum virgatum*) but is not effective on softwoods (Peter and O. 1985). The Solvent Fractionation Process has a number of advantages in comparison to more conventional pulping processes (Bozell, O'Lenick et al. 2009). These include:

1. The presence of organic solvents reduces the viscosity of the pretreatment medium, improving penetration into the biomass and facilitating a more efficient removal of lignin.
2. The presence of solvent retards the redeposition of lignin onto the other biomass components after separation is complete. Furthermore, redeposition can be effectively eliminated through pH control. More effective lignin removal also lessens the amount of lignin recondensation and molecular weight increase.
3. Organosolv cellulose is easier to purify. This is important in the paper industry as a solution for environmental issues associated with pulp bleaching, but also to the chemical industry, as it frequently requires starting materials of high purity.
4. The process is elaborate, and recovery of the solvent components can be carried out efficiently.
5. The process is economic at small scales, and offers easy access to all components of the starting biomass feedstock. This may be of particular value to production of a chemical at reasonable scales.

The (NREL) National Renewable Energy Laboratory's (CF) Clean Fractionation Process is a contribution to the Organosolv technology. The CF process differs from

other Organosolv processes in that the ternary solvent mixture remains as single phase throughout the entire pulping process (see Figure 1).

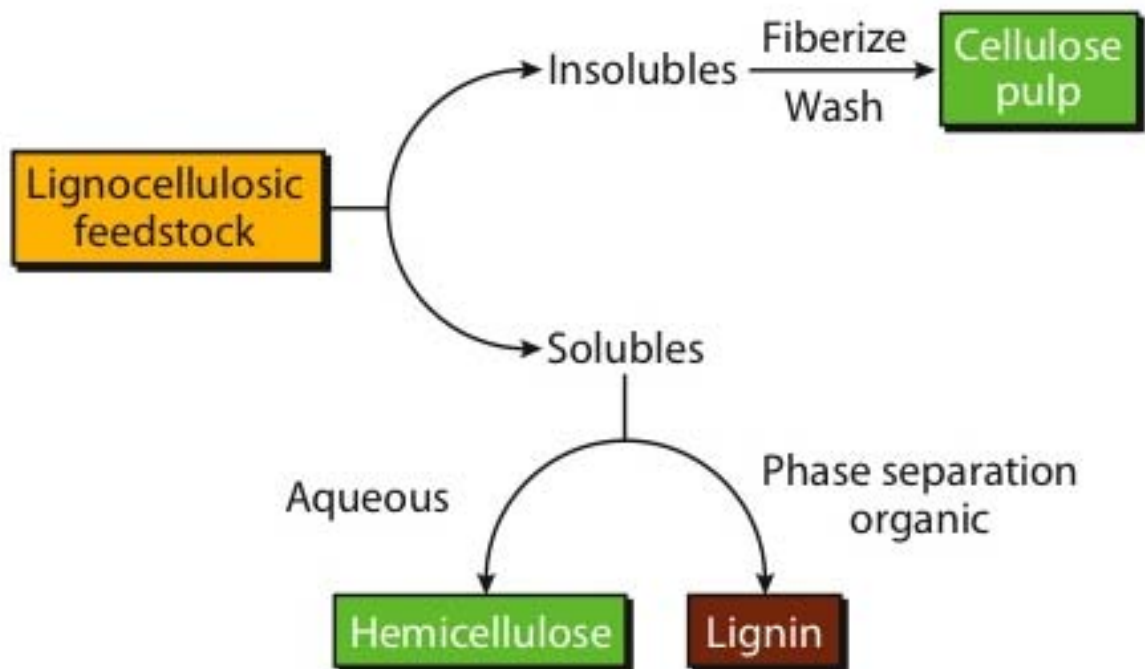


Figure 1: The NREL Clean Fractionation Process (Christensen 2008)

The process treats the biomass source with a ternary mixture of methyl isobutyl ketone (MIBK), ethanol and water in the presence of an acid promoter. Standard conditions use 16/30/50 mass ratio of MIBK/EtOH/H₂O for 56 minutes at 140°C in the presence of 0.05 – 0.2M H₂SO₄. The solvent mixture selectively dissolves the lignin and hemicellulose components, leaving the cellulose as an undissolved material that can be washed, fiberized, and further purified. The soluble fraction containing the lignin and the hemicellulose is treated with water, causing phase separation to give an organic phase containing the lignin and an aqueous phase containing the hemicellulose. CF is a very general process, and can be used for fractionation of a wide range of biomass feedstocks including corn stover, newsprint, bagasse, corn fiber, miscanthus and rice straw. Moreover, the process is not limited to the single solvent mixture described. Several different solvent combinations give single phase mixture (Table 1: Typical CF Solvent Compositions), however, the great majority of the work has been carried out using -1 solvent (Bozell, O'Lenick et al. 2009).

Table 1: Typical CF Solvent Compositions (percents are mass percents)

Solvent Classification	% MIBK	% EtOH	% H ₂ O
+2	62	27	11
+1	44	32	24
0	28	35	37
-1	16	34	50
-2	7	30	63

3.1 Method

The experiment was a Matrix of 3 different temperatures at 3 different acid concentrations as promoter, with a -1 solvent (see Table 1) and the biomass used was switchgrass. The temperatures chosen are 120, 140 and 160°C with 0.025 M, 0.05 M and 0.1 M H₂SO₄ as promoter. The time of the reaction was exactly 56 *min*. The fractions (Black-Liquor and Cellulose) have been separated and quantified. For the separation of the Black-Liquor 4 different methods have been used, these methods have been developed during the matrix in small-scale experiments.

The qualitative analysis methods are 2D NMR for lignin, FTIR for lignin and cellulose, HPLC for hemicellulose and Kappa for cellulose. These are still in progress and will not find place in this report.

For the mathematical analysis SPSS, JMP and Excel has been used.

3.1.1 Run

A run (Solvent Fractionation Process) can be split in a vacuum phase, a filling phase, a heat-up phase and the flow phase. In the vacuum phase the switch grass collapse and the vacuum improves the penetration of the SG with solvent. After 20 *min* the fill tank will be opened to fill the reactor to the outlet of the reactor. The height of filling has been tested and is controlled by the amount of solvent introduced into the vacuum trap (100 *ml*).

The next phase is the heating; this usually takes 40 *min* to come to an average core temperature of 140 °C. When three heaters are at temperature and the fourth is 5 °C below the reaction temperature, the pump will be started. The pressure before starting the pump is called equilibrium pressure (P_{eq}). The BadgerValve will open at

$$P_{eq} + offset = ValveOpening$$

The offset is usually set to 10 *psi*. For starting the pump the stroke rate has to be set to 25 s^{-1} to decrease the time to flow. At *ValveOpening pressure* - 1 *psi* the stroke rate will be set back to the original rate (e.g. 10 s^{-1})

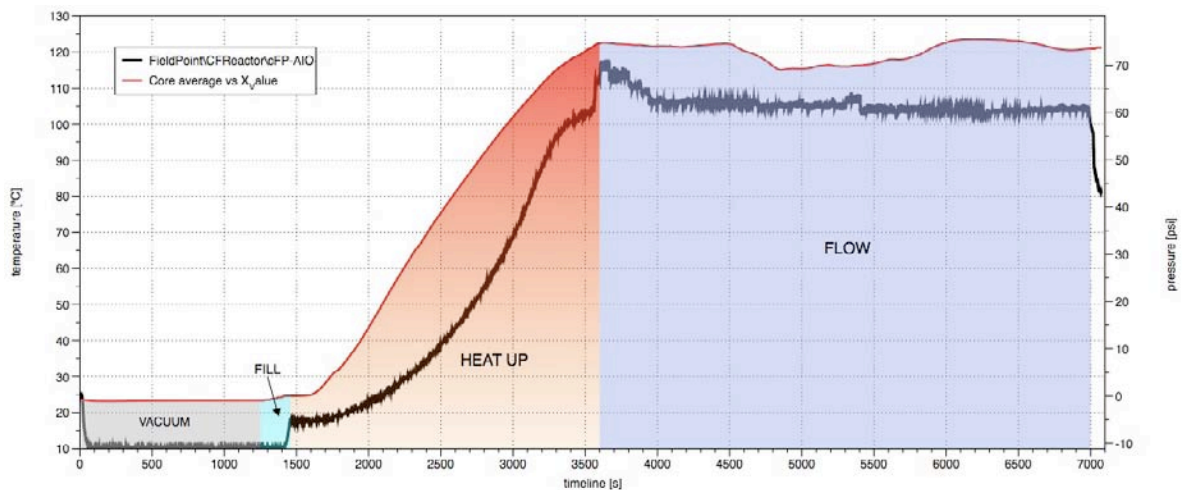


Figure 2: Four phases of CF run

As soon as the flow starts the timer is set to 56 *min*. During these 56 *min* the flow is measured 5 times and should be about 3.5 *l/run* this equals 3.75 *l/h*. After the 56 *min* the heaters were turned off and the BL drain thru a valve into the collection pot.

To get an overview of the settings, the equilibrium pressure at the specific temperatures has been correlated and is shown in the following graph (see Figure 3).

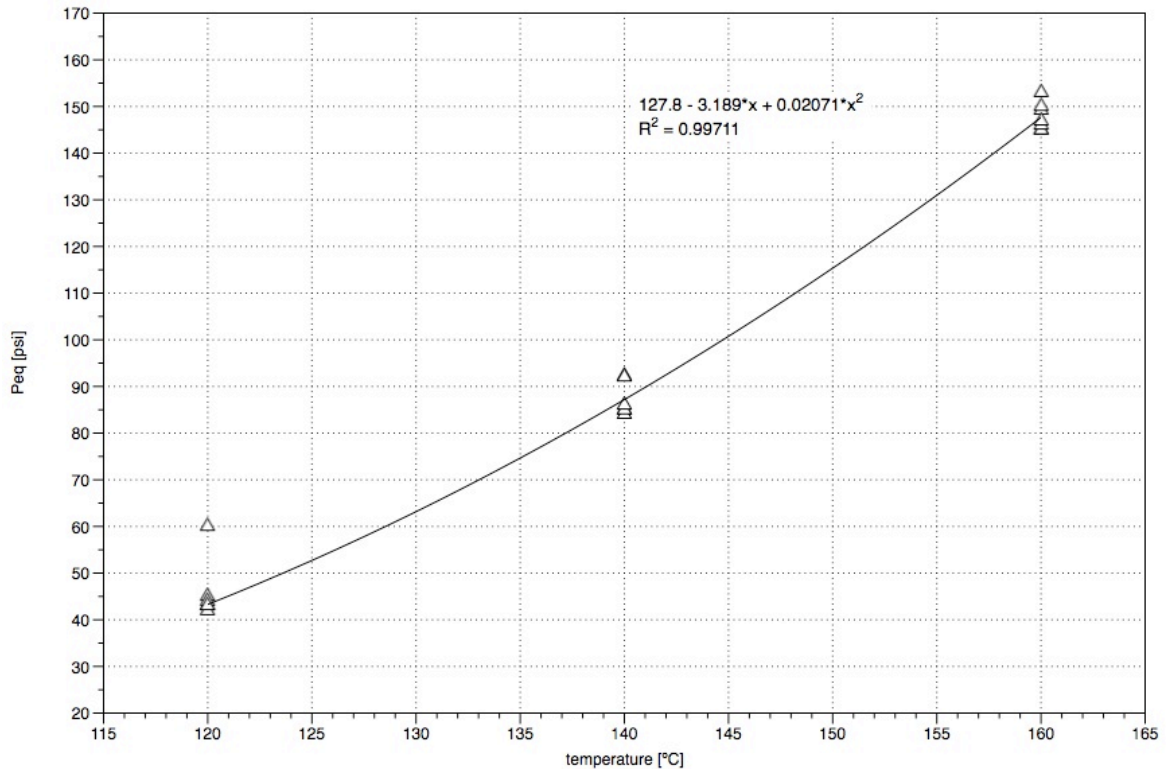


Figure 3: correlation between temperature and P_{eq}

3.1.2 Postprocessing

There are 2 fractions after the run, the cellulose in the reactor and the BL in the drain-pot.

3.1.2.1 Cellulose

To make the fiberization of the cellulose easier, 3 l of DI H₂O were added before blending it. The next step is a kind of a displacement-press. The cellulose gets washed with DI water for 2h in a Buchner funnel under vacuum. Then the cellulose gets dried for further 2 hours under pressure. This cake of cellulose gets weighed and a small sample of about 8 g will be used to measure the content of solids (TAPPI-T412 2002)

3.1.2.2 BL

For the separation of the Black-liquor four different methods have been developed. The initial separation developed by CJ O'Lenick is called method 1 and all other methods are based on this. The methods are very similar regarding the timing and ratio of BL and DI or MIBK.

The basic procedure is: 25 % of MIBK or DI H₂O were added to the BL into the separation funnel (4L). Then the mixture gets shaken for 1 *min* and the separation funnel gets vented. After this the mixture separates for 30 *min* and then the AQ phase will be drained off. The mixture gets further 5 minutes for separation and the AQ phase will be drained again. The solvent phase (top layer) goes to the lab for Celite filtration process and a further separation process.

3.1.2.2.1 Method 1

Only one separation process with DI H₂O has been used, as mentioned above. Solvent is called "lignin solvent 1".

3.1.2.2.2 Method 2

An additional separation of the AQ phase, using MIBK instead of DI H₂O. This solvent is then called "lignin solvent 2".

After the separatory funnel treatment (method 1), the AQ (aqueous phase) was very dark and there was also no visible phase separation. This was the reason why an additional MIBK separation step with the liquid phase has been tried.

The experiment looks like this:

1. adding 100ml first aqueous phase + 25% MIBK into the separation funnel
2. wait 30 *min*
3. drain the separated phases
4. collect the solvent phase

After adding the MIBK to the First Aqueous Phase the organic layer separated very fast and clear (see Figure 4).



Figure 4: test separation with MIBK

According to this result all the aqueous phase has been separated with an additional MIBK step.

3.1.2.2.3 Method 3

The Solvent 2 lignin of Method 2 gets 2 additional DI H₂O drying steps by adding 25% of DI H₂O to the Solvent 2 lignin into the separation funnel and a reduced separation time of 15 *min* instead of 30 *min*. This solvent is then called “reduced lignin solvent 2”.

The 2 washing steps reduced the volume from 1610 *ml* to 1310 *ml* and this decreases the rotary evaporator drying time.

3.1.2.2.4 Method 4

This method is similar to method 2, but instead of DI H₂O, MIBK is used in both separation processes. This method leads to a consistent amount of solvent and a very easy drying step of the lignin. Solvents are called “lignin solvent 1” and “lignin solvent 2”.

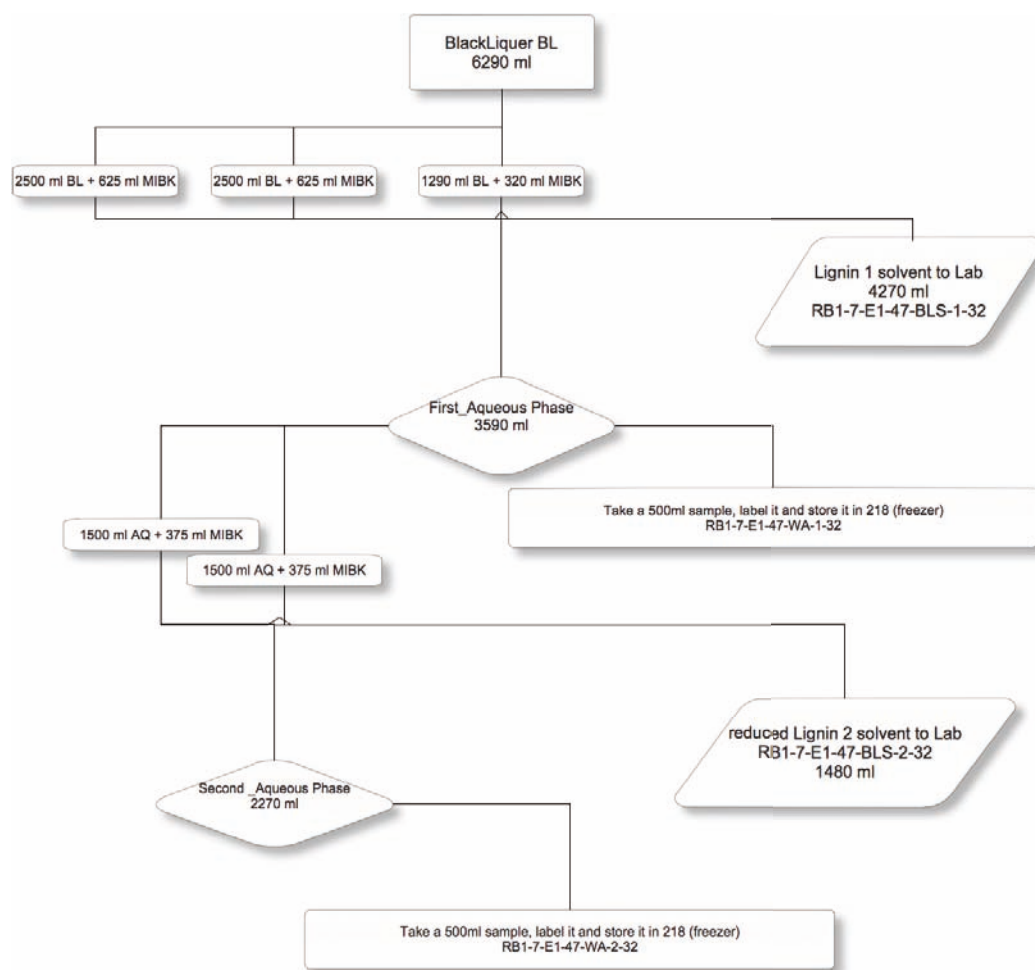


Figure 5: Flowchart of separation method 4

3.1.2.3 Hemicellulose AQ

After the separation a sample (500ml) of both AQ (aqueous) phases, will be stored in the freezer for further analysis. HPLC will give a qualitative and quantitative result of the composition of the Hemicellulose in the AQ phase (in progress). Ash and acid soluble lignin will be found in this phase (Fengel and Wegener 2003).

3.1.2.4 Lignin Solvent

The phase separation of the solvent phase and the aqueous phase is not always clear and there is a kind of emulsion layer between the phases. This emulsion can be cracked, by filtering it through Celite (Diatomaceous earth), providing additional aqueous and organic phase.

After the Celite filtering and additional separation of the solvent, the organic phase is treated with a Rotavap to remove solvents (at 65 – 70 °C), and solids are then dried

by ether addition and evaporation (50ml ether at 55 - 60°C). The ether-drying step is a triteration, to remove oil parts of the lignin. To get comparable samples a small amount of 2g has been used to determine the content of solids. Therefore the procedure of (TAPPI-T412 2002) has been changed. The TAPPI is based on cellulose, because of the lignin a drying temperature of 65 °C was used.

3.1.2.5 Reducing MIBK in separation

An additional separation experiment has been started with 500 ml of the BL. The 500 ml have been split to a 250 ml sample (experiment 1) and a 240 ml sample (experiment 2). Instead of adding 25% of MIBK, 20% have been added into the separation funnel. Than the samples have been shaken for 1 *minute* and 30 *minutes* of separation before draining. The AQ phase of the experiment 1 has been treated with additional 20 % of MIBK while the AQ phase of the experiment 2 has been treated with DI H₂O. Both samples have been rotavaped and dried in the vacuum oven for 3 days at 65°C and -20 *inHg* vacuum. The tare weight of the flasks and the final weight after drying gave a very exact amount of separated lignin. These amounts have been divided by the amount of BL to compare them with the standard separation of the BL.

$$\frac{\text{final_weight_after_drying}[g] - \text{tare_weight_flask}[g]}{\text{amount_of_BL}[ml]} * 100 = \text{ratio_of_recoveredLignin}$$

The results show that a reduction of MIBK from 25% to 20% results in a reduction of recovered lignin of 0.1%. By changing the 2nd separation process from MIBK to DI the ratio_of_recoveredLignin reduced about 0.3%. The collected samples have to be analyzed with 2D NMR to see the qualitative difference. If the quality is the same a reduction could reduce the amount of MIBK used for separation.

3.2 Results

These results do summarize the analysis done so far on the cellulose and on the lignin.

3.2.1 Cellulose

It turns out that the break down of the cellulose is correlated with the temperature and the acid concentration. The higher the acid concentration, the better the break down. The break down also increased with higher temperature. On Figure 6 the dried cellulose shows a lot of fibrous material, looks more like a fiberboard than like cellulose. There are several unreacted switch grass stems (see Figure 6 left picture) in the cellulose, that means that there is lignin inside and the low temperature in combination with low acid is not able to break down the SG.



Figure 6: very fibrous material on the left pic (120°C / 0.025 M acid) and ++ breakdown on the right picture (140°C / 0.1 M acid)

It turns out that the acid concentration has a much higher impact on the break down of the cellulose than the temperature. On almost all runs (temperatures) with low acid concentration the break down was very bad, while the runs with 0.1 M acid had a good breakdown.

The yield of cellulose ranged from 26.25 mass % to 52.43 mass %. The quality of the breakdown of the cellulose was classified into 4 groups, where 1 is very good break down and 4 is bad break down. The classification has been done visually, however the correlations between acid concentration of the catalyst and the breakdown are very good on the 120 °C and 140°C runs. On the 160 °C run the

effect of the acid concentration was a very dark cellulose, this could be some lignin compounds recondensed to the cellulose (see Figure 7).



Figure 7: cellulose of a 160 °C run with 0.1 M acid

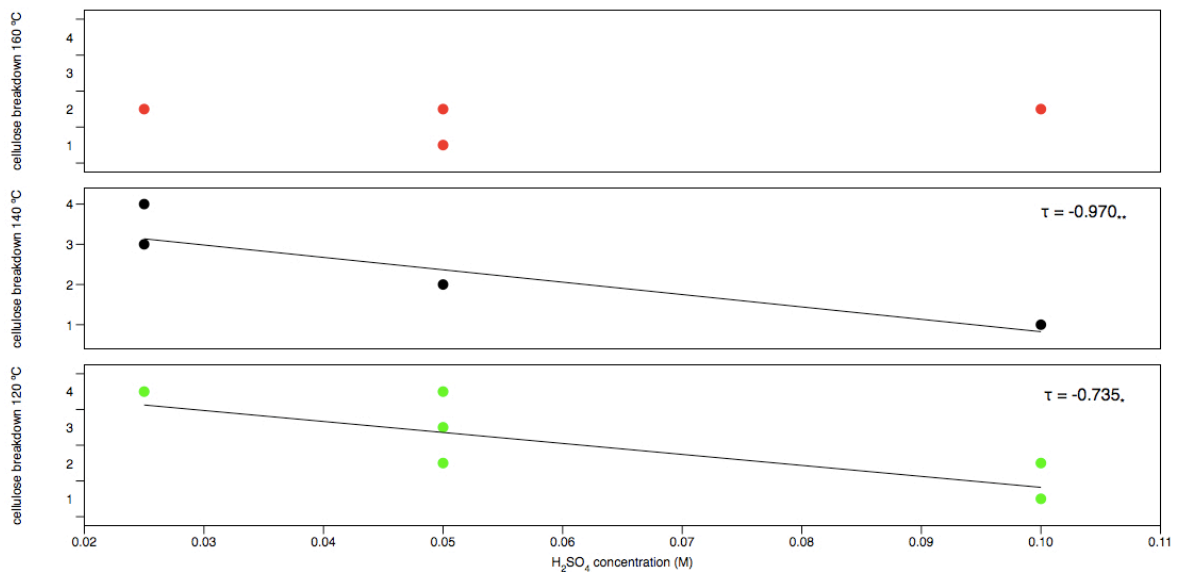


Figure 8: acid concentration vs. cellulose breakdown at the specific run temperatures (120, 140 and 160 °C)

For calculating the correlation between the breakdown and the acid concentration, the Kendall – Tau correlation has been used. This correlation is used for classified data, because of the missing distance of the variables.

The effect of temperature on the cellulose breakdown was very low; there was no significant correlation between temperature and breakdown.

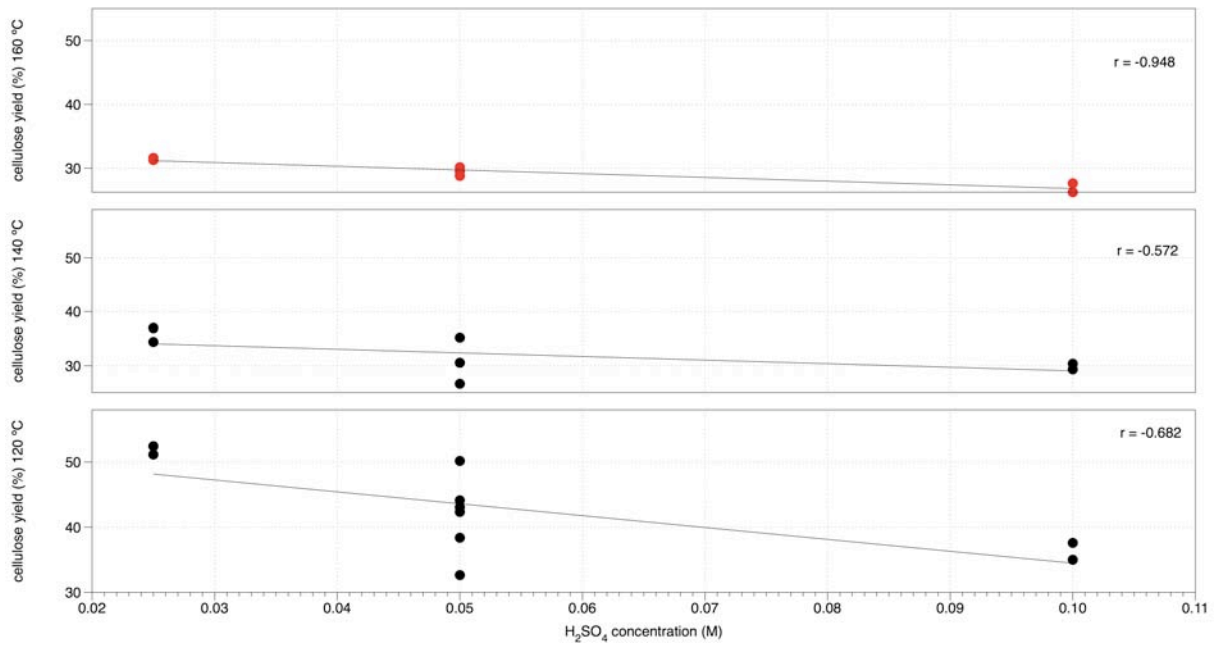


Figure 9: correlation between acid concentration (M) and cellulose yield (%)

The cellulose yield was not that much affected by the acid concentration. There is a correlation but the impact of the temperature is much higher (see Figure 10).

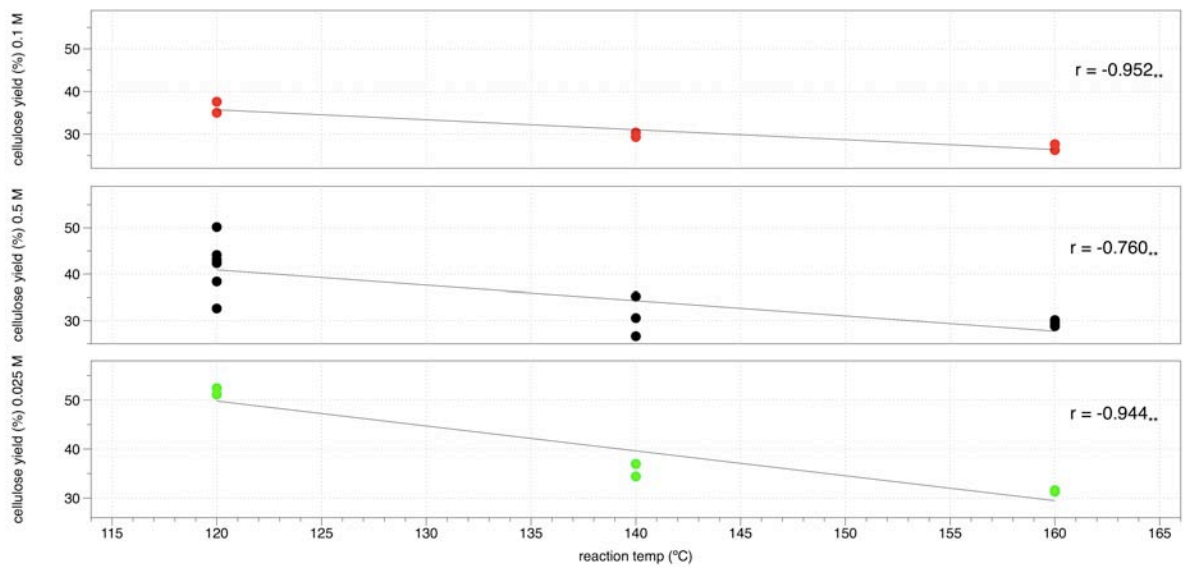


Figure 10: correlation between reaction temp (°C) and cellulose yield (%)

The impacts of acid concentration and run temperature are shown in the following graphs.

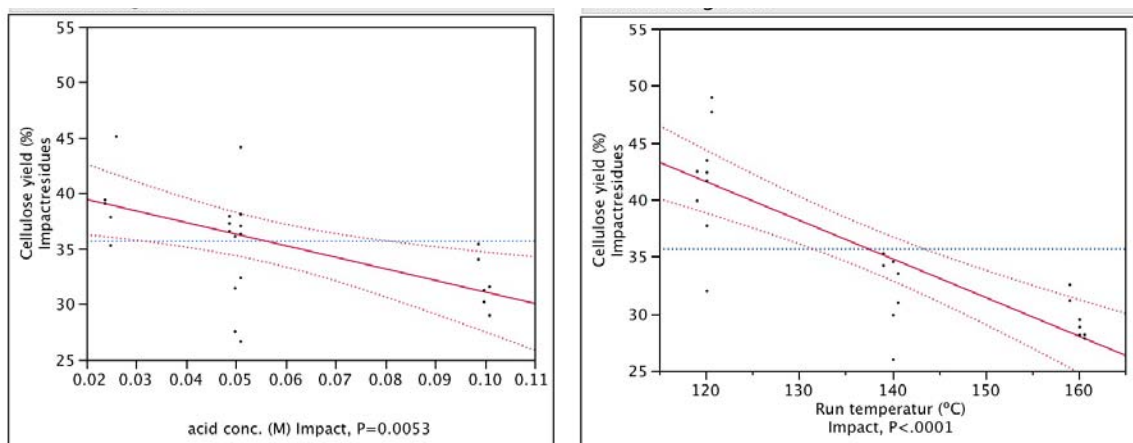


Figure 11: impact of acid concentration (%) and Run temperature (°C) at the Cellulose yield (%)

The analysis of the cellulose fraction is yet not finished and a Kappa-number or FTIR spectra will give more information about the quantity and quality of the cellulose. Fact is that a too low acid concentration does not break down the cellulose and there must be lignin left inside, on the other hand the highest acid concentration combined with high temperature recondenses the cellulose and the quality decreases. The acid concentration has not a relevant impact to the cellulose yield compared to the temperature. Just at the 120 °C runs the impact of the acid concentration is significant (see Figure 9).

3.2.2 Lignin

Table 2: content of solids after drying

	content of solids lignin 1 (%)	content of solids lignin 2 (%)	content of solids cell (%)
n	25	13	24
\bar{x}	94.0776	94.60	22.0589
min	88.7	91	18.3
max	97.67	98	25.19
s	2.4588	2.301	1.4068

It turned out that for the separation of the BL, method four gives the best result in drying and amount of lignin.

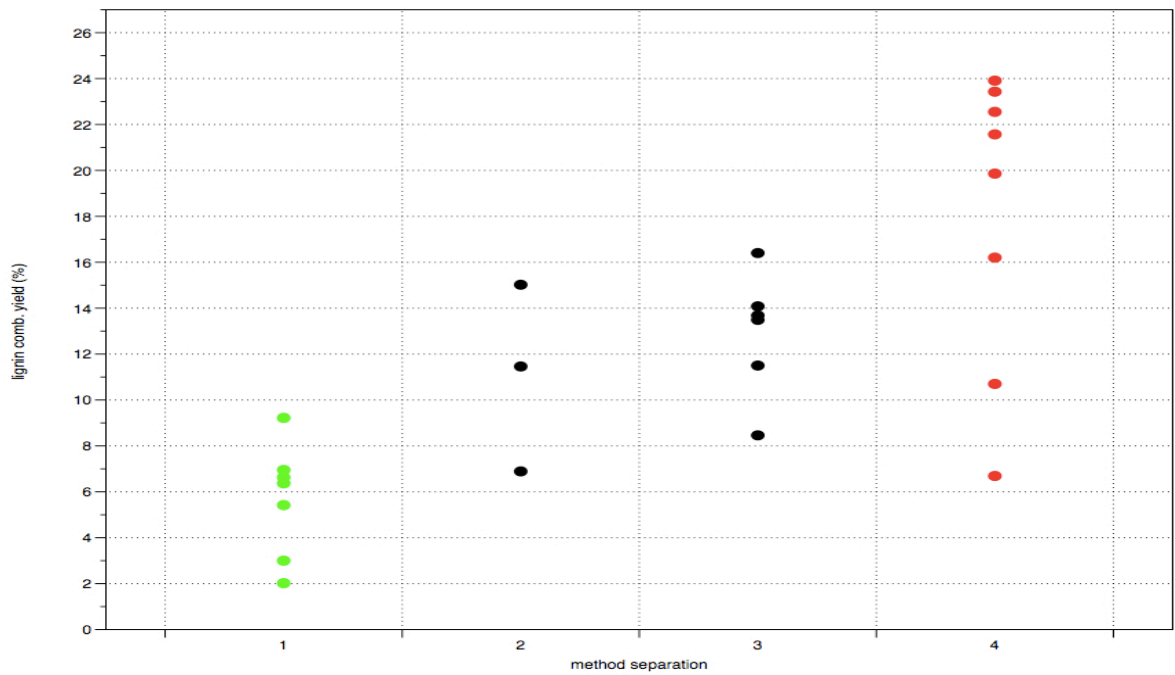


Figure 12: lignin yield (%) vs. methods (1, 2, 3 and 4)

Figure 12 shows the yields separated with the 4 different methods. Method 2 and 3 are similar regarding the separation so they are in the same color at the plot. Separation method 1 has just one lignin and that leads to the smallest amount of lignin (below 10 %). The MIBK separates almost all lignin in the first step. The 2 outliers in the region between 6 % and 11 %, are runs with 120 °C and 0.025 M acid.

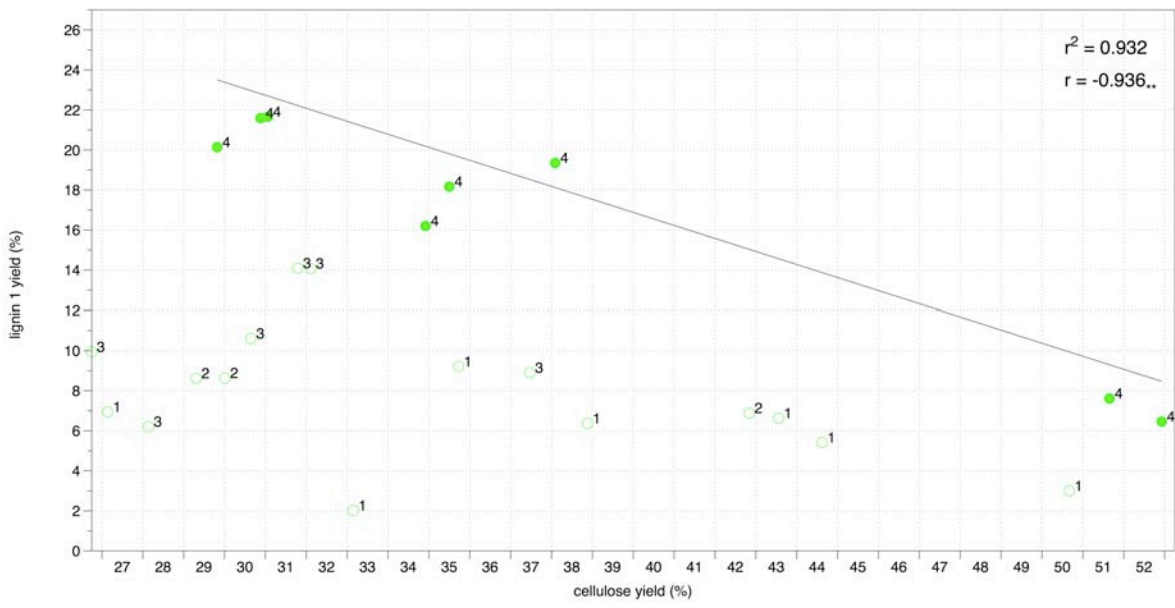


Figure 13: lignin yield (%) vs. cellulose yield (%)

The correlation between cellulose yield and lignin yield is also very high, when the other separation methods are excluded (see Figure 13). So for better statistic on the data some of the runs with a different separation method than method 4 have to be repeated.

Qualitative analysis is important to find the best method for separation. The highest switchgrass lignin yield of 24 % is higher than the lignin yield found in the literature which is 17.2 % (Qin, Mohan et al. 2005). This leads to the presumption that there are also cellulose decomposition products included like furfurals, furans and decomposed sugars. These decomposition products are soluble in the organic phase and since the separation method 4 is used the decomposition products are collected with the first lignin.

According to Table 3 the cellulose content of switchgrass is about 37.10 %, which is looking at method 4 at Figure 13, almost the region of 18 – 19 % of lignin yield.

Table 3: Cell wall constituents of switchgrass (Qin, Mohan et al. 2005)

Constituent	% By bone dry weight base
Cellulose	37.10
Hemi cellulose	32.10
Fixed Carbon	13.60
Lignin	17.20

Run #37 and run #36 are in the region of 37 % cellulose yield and 18 % lignin yield , both are 120°C runs with 0.1m acid. Run #30 (see Figure 13; 35 % cellulose and 16 % lignin) is a 140 °C run with 0.025 M acid, but there were problems with the pump during the run. The switchgrass was sitting in the solvent for 45 min at a temperature of 80°C. The increase of presoaking time with low acid gave the save result regarding quantities, like a high acid run without presoaking time. It leads to the presumption that high acid and low temperature are the best combination regarding to the yields (quantities) but also the time could have a big impact. Further experiment should be carried out to figure out how the time affects the yields.

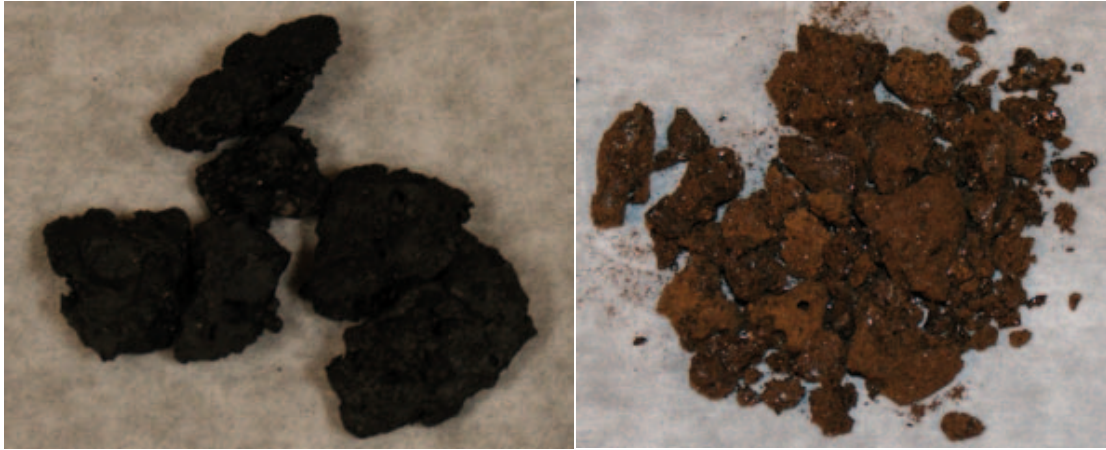


Figure 14: left lignin run # 37; right lignin run # 30

However the yields are very similar on run #30 and #37, the color is quiet different. The qualitative analysis will give information of the differences between these two lignins.

4 Reactor

The reactor in use at UT is a flow through design. Biomass is loaded into the reactor. Solvent is pumped into the reactor from the feed tanks, and heated via controllers in the electrical enclosures. Solvent is pumped through the reactor for about 1 hour at the selected temperature, and collected at the collection tank. At the completion of the reaction, the remaining solvent in the reactor is drained into the collection tank. Current control of solvent flow is carried out using LabVIEW software to control a output valve in the flow system.

4.1 Material

In Figure 15, the reactor system is shown. The small reactor on the right side was finished regarding the fractionation process. Only the data acquisition and the temperature reading had to be done manually. The big reactor was 75% finished at the start of the internship, the complete wiring and a few parts of the plumbing were missing. There were also problems with pressure fluctuations of about 10 to 50 psi caused by the pump that should be solved. A further problem of pressure spikes also had to be solved.

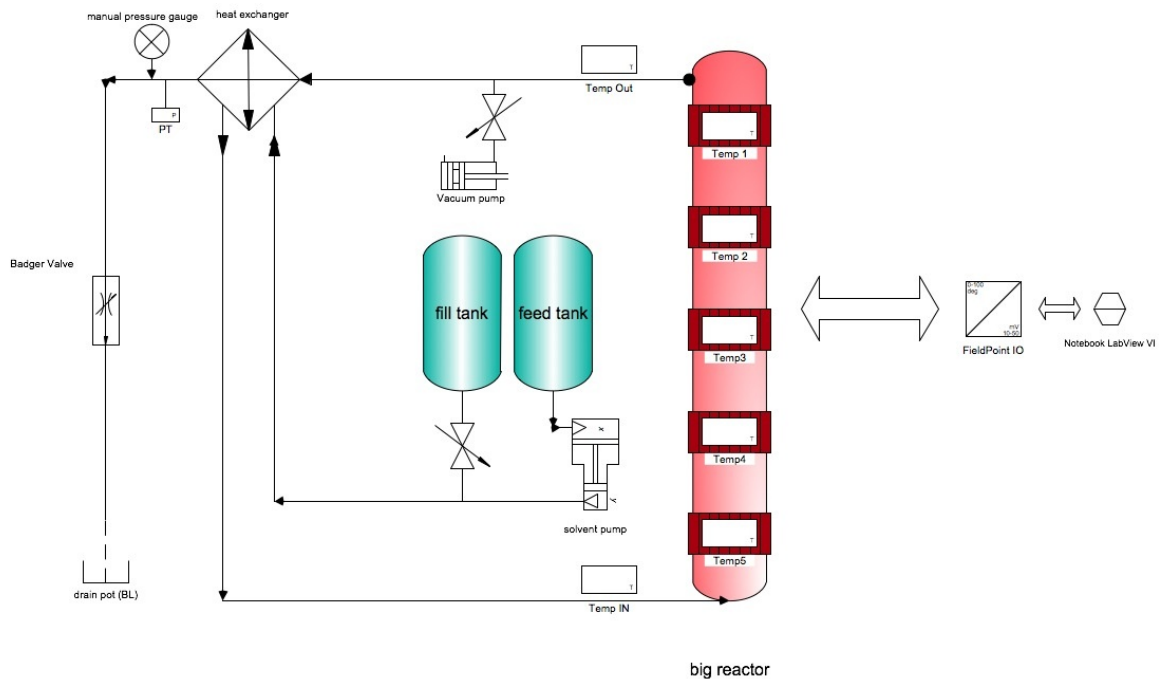


Figure 15: Clean Fractionation Reactor schematic

The reactor is a very simple system. There is a vacuum pump (GAST DOA-P707-AA Pump) for vacuuming the air out of the reactor for 20 *min*. Then the reactor gets filled, with solvent by opening a valve. After the reactor is filled the heaters heat the system up to a specific temperature. When the temperature is reached the pump starts to push solvent thru the reactor. The amount of solvent is controlled by the BadgerValve, which is controlled by LabVIEW. An approximate amount of 3.5 l is used for filling and further 3 l of solvent are used for pumping thru the system (small reactor). Additional information, to carry out the run, is documented in the reactor log sheet. Both reactors use the same vacuum pump, BadgerValve and solvent pump.

4.1.1 Reactor material

The reaction chamber of the reactor is made of Hastelloy, which is a trade name of the company Haynes International, Ltd. This metal is resistant against several aggressive chemicals. The alloy consists of Ni and Mo, additional information about physical properties are in (Haynes International 2009).

Table 4: capacity of reactors

	small reactor	big reactor
height [in]	44	66
ID [in]	3	4
OD [in]	3.5	4.5
Hastelloy [kg]	17	34
Solvent for filling to the outlet [l]	3340	8820
Switchgrass [g]	270	700

4.1.2 Heater bands

For heating the small reactor 4 and for the big reactor 5 heater bands (Watlow) are used. The required power is 365 W per heaterband. This equals 3.32 A per heaterband according to the following equation when the voltage is 110 V. The installed power for the small reactor is:

$$4 * 375W = 1500W$$

The installed Power for the big reactor:

$$5 * 375W = 1875W$$

The following equation and specific heat capacities, give the power needed to heat-up the reactor:

$$Q = m * c * \vartheta$$

$$c_{Hastelloy} = 0.4[J/g \cdot K]$$

$$c_{Water} = 4.1855[J/g \cdot K]$$

$$c_{Switchgrass} = 1.38[J/g \cdot K]$$

Assuming that the small reactor is filled with 3.340 l of water and 270 g of switchgrass, and the big reactor is filled with 8.8 – 8.9 l of water and 700 g of switchgrass, the mass of metal to heat up at the small reactor is about 17 kg and for the big reactor it is about 34 kg. The heat-up time from 20 – 160 °C assumend is 38 min. The installation power needed for the small reactor will be 1434 W and the power needed for the big reactor will be 3434 W.

The heater installation on the big reactor fails completely the power demands for a run. The suggestion is to double the amount of heaters, this would lead to an installed power of 3750 W.

In the calculation for the needed power, water has been used instead of the solvent -1 mixture. The specific heat capacity of the solvent is much lower, however the system is at the very low end of installed power. This calculation also does not include the heat loss reduction related to the insulation, where the surface temperature of the insulation is about 62°C.

Table 5: installed power status 07-20-09

	small reactor	big reactor
heaters	4	5
power/heater	375 <i>W</i>	375 <i>W</i>
installed power	1500 <i>W</i>	1875 <i>W</i>
installed power needed	1435 <i>W</i>	3435 <i>W</i>

Table 6: suggested power installation

	small reactor	big reactor
heaters	5	10
power/heater	375 <i>W</i>	375 <i>W</i>
installed power	1875 <i>W</i>	3750 <i>W</i>
installed power needed	1435 <i>W</i>	3435 <i>W</i>

For installing 3435 *W* heater-power the circuit box has to be changed from 110V to 220V with 2 phases. Therefore one Omega controller has to control 2 heater-bands and the power supply has to be split into 2 circuits. Where 6 heaters are connected to the first phase and the other 4 heaters + the controllers are connected to the second phase.

4.1.3 BadgerValve

Badger meter Type 766 BLRA Modell 4 is an Air-to-Open Positioner Actuator and has an integral, top-mounted positioner. It operates pneumatically with a spring opposed diaphragm. The operation is quite simple. Two air lines are required one to provide instrument signal and on to provide supply air. The amount of air is determined by the springload. The positioner, when in operation, will constantly bleed unused supply air (BadgerMeter 2001).

The BadgerValve is controlled by an ITT Conoflow Model GT4108EB. This controller converts a input signal of 4-20 mA DC to a proportional 3-27 PSIG output

signal(ITT 2009). The input signal is connected to the FieldPoint Module and controlled by LabView.

4.1.4 Solvent pump

The Type of solvent pump used in the reactor is a Williams CR P500V225 CR TC. The pump is again controlled by air from a Controller (see Figure 16).

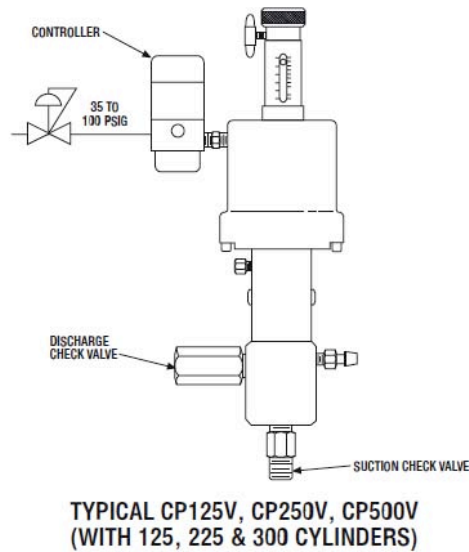


Figure 16: Solvent pump reactor

There are 2 ways of controlling the pump. Both are manual settings and there is no way, with this equipment, to control it by LabView. The first setting is called stroke length and is the volume in *ccm* per stroke. It is an adjustment directly at the pump. The second setting is called stroke rate which can be manually adjusted at the Oscillamatic[®] controller. The stroke rate is an unscaled factor from 0 – 100 which depends on the supply air pressure. The default setting for the small reactor is about 1.5 *ccm* stroke length and 10 stroke rate with a supply pressure of 60 *psi*. This leads to a flow of 2.2 l/run to 3.4 l/run depending on the density of the switchgrass.

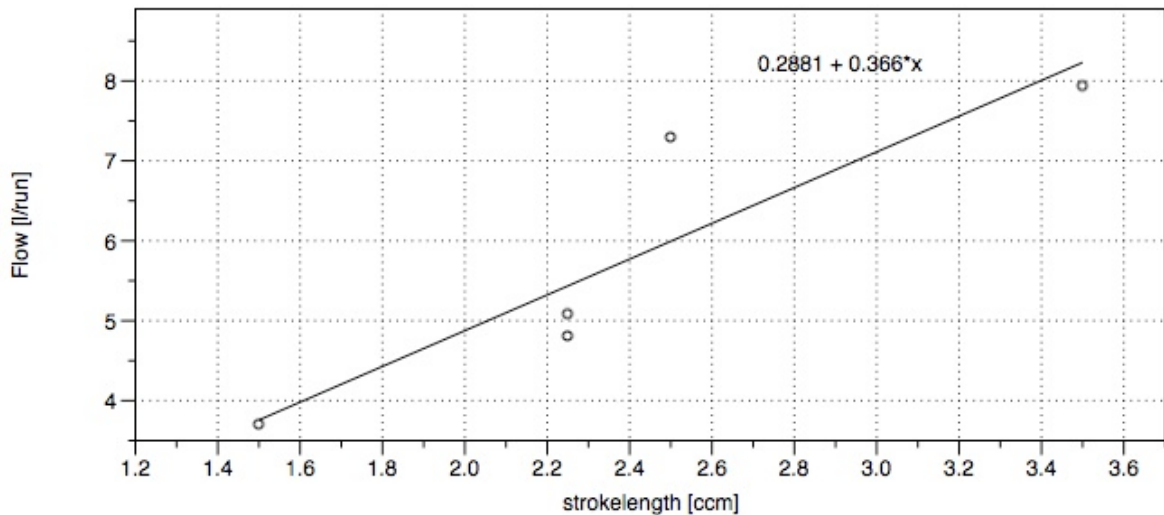


Figure 17: Flow adjustment with a stroke rate of 10 s^{-1}

It turned out that the stroke rate of 10 s^{-1} gives the best result regarding the pressure fluctuations. The rate is only changed in the beginning to increase the speed of reaching the offset point.

4.1.5 Backpressure Valve

To get rid of the fluctuations a Backpressure Valve as been installed. The Type of the Valve is a RL3 Pressure Valve from Swagelok (Swagelok 2009). On suggestion of Patty Mc Donald from Swagelok the Backpressure Valve was set to 200 psi with the following test setup (see Figure 18).

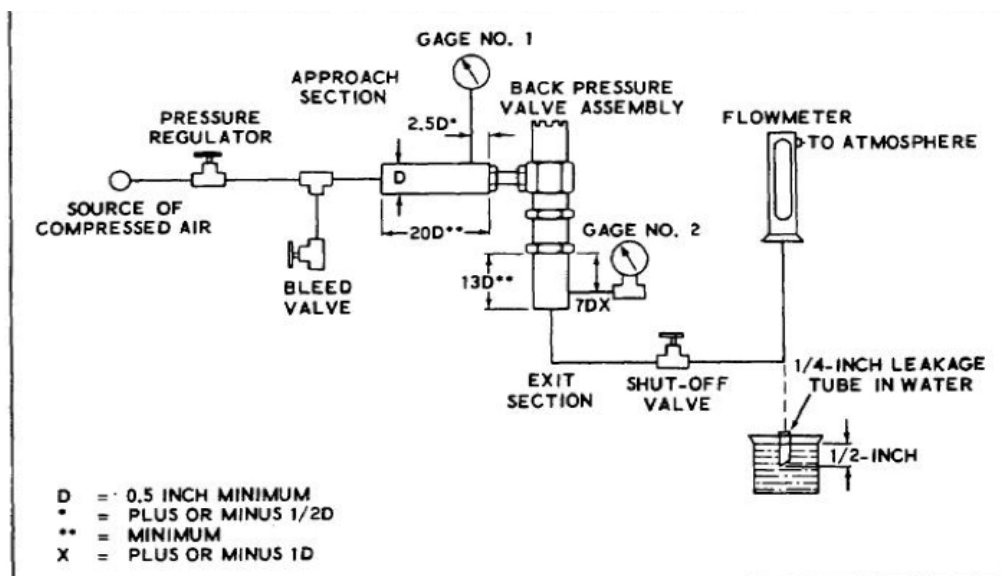


Figure 18: Back Pressure Test Set-Up (Publishing 2009)

The third method to reduce fluctuations is changing the opening of the BadgerValve by controlling the valve factor (see Figure 19). The BadgerValve opening (on the right) should be about 60%. Also, the pressure of the air supply for the pump can be a reason for fluctuations, if the pressure is lower than 60 psi the pump works too soft and this results in fluctuations.

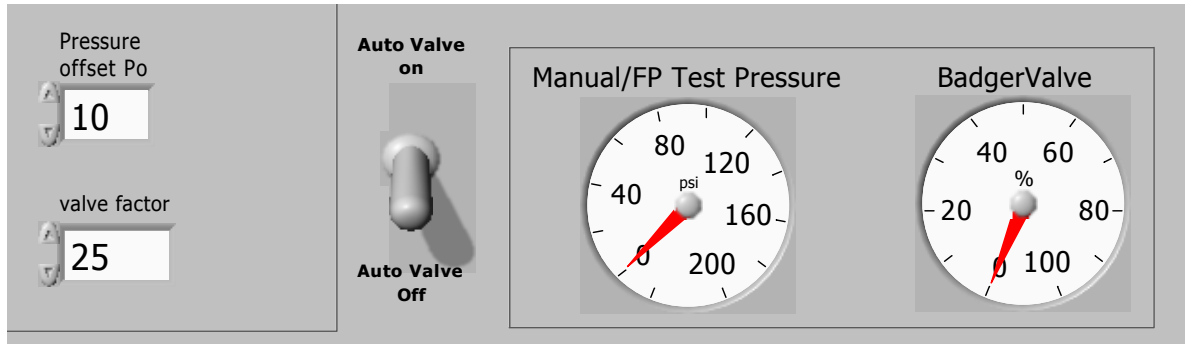


Figure 19: Valve settings on VI

4.2 Recommendations

The reactor is a working tool, for running the experiments and collecting data. The small reactor is already there to make reproducible runs. The big reactor has to be upgraded with heaterbands and 220 V power supply and then the experiments can start. However to get more data and make the process easier some recommendations find place here.

LabVIEW should control the temperature; therefore Relay modules from NI FieldPoint have to be installed. The system can be controlled better by LabView and different temperature profiles can be used for a run.

A Flowmeter displays the flow over the run continuously and the process can be controlled by this data.

The tank system has to be upgraded to make a run easier. Therefore a air supply with about 10 psi give a continuous pressure to the feed tank, to make the start of the pump easier.

Purging has to be developed, at the moment too many connectors have to be dismantled to purge the system. This leads to leaks, caused by mechanical abrasion.

A NIR at the outlet of the reactor could also give an excellent control element for running the reactor at an optimum yield.

Also, a combination of both systems (big and small reactor), where the small reactor serves as a pre-heater and pressure reservoir, can be a direction. This could speed up the process and avoid all kind of pressure fluctuations. A predictable stream and flow rate would also be a result of this setting.

5 LabView

5.1 Material

LabVIEW (short for Laboratory Virtual Instrumentation Engineering Workbench) is a platform and development environment for a visual programming language from National Instruments. The graphical language is named "G". Originally released for the Apple Macintosh in 1986, LabVIEW is commonly used for data acquisition, instrument control, and industrial automation on a variety of platforms including Microsoft Windows, various flavors of UNIX, Linux, and Mac OS X. The latest version of LabVIEW is version 8.6.1, released in February of 2009 (National 2009).

5.1.1 Dataflow programming

The programming language used in LabVIEW, also referred to as G, is a dataflow programming language. Execution is determined by the structure of a graphical block diagram (the LV-source code) on which the programmer connects different function-nodes by drawing wires. These wires propagate variables and any node can execute as soon as all its input data become available. Since this might be the case for multiple nodes simultaneously, G is inherently capable of parallel execution. Multi-processing and multi-threading hardware is automatically exploited by the built-in scheduler, which multiplexes multiple OS threads over the nodes ready for execution (National 2009).

5.1.2 Graphical programming

LabVIEW ties the creation of user interfaces (called front panels) into the development cycle. LabVIEW programs/subroutines are called virtual instruments (VIs). Each VI has three components: a block diagram, a front panel, and a connector panel. The last is used to represent the VI in the block diagrams of other, calling VIs. Controls and indicators on the front panel allow an operator to input data into or extract data from a running virtual instrument. However, the front panel can also serve as a programmatic interface. Thus a virtual instrument can either be run as a program, with the front panel serving as a user interface, or, when dropped as a node onto the block diagram, the front panel defines the inputs and outputs for the

given node through the connector pane. This implies each VI can be easily tested before being embedded as a subroutine into a larger program.

The graphical approach also allows non-programmers to build programs simply by dragging and dropping virtual representations of lab equipment with which they are already familiar. The LabVIEW programming environment, with the included examples and the documentation, makes it simple to create small applications. This is a benefit on one side, but there is also a certain danger of underestimating the expertise needed for good quality "G" programming. For complex algorithms or large-scale code, it is important that the programmer possess an extensive knowledge of the special LabVIEW syntax and the topology of its memory management. The most advanced LabVIEW development systems offer the possibility of building stand-alone applications. Furthermore, it is possible to create distributed applications, which communicate by a client/server scheme, and are therefore easier to implement due to the inherently parallel nature of G-code (National 2009).

5.1.3 Benefits

One benefit of LabVIEW over other development environments is the extensive support for accessing instrumentation hardware. Drivers and abstraction layers for many different types of instruments and buses are included or are available for inclusion. These present themselves as graphical nodes. The abstraction layers offer standard software interfaces to communicate with hardware devices. The provided driver interfaces save program development time. The sales pitch of National Instruments is, therefore, that even people with limited coding experience can write programs and deploy test solutions in a reduced time frame when compared to more conventional or competing systems (National 2009).

In terms of performance, LabVIEW includes a compiler that produces native code for the CPU platform. The graphical code is translated into executable machine code by interpreting the syntax and by compilation. The LabVIEW syntax is strictly enforced during the editing process and compiled into the executable machine code when requested to run or upon saving. In the latter case, the executable and the

source code are merged into a single file. The executable runs with the help of the LabVIEW run-time engine, which contains some precompiled code to perform common tasks that are defined by the G language. The run-time engine reduces compile time and also provides a consistent interface to various operating systems, graphic systems, hardware components, etc. The run-time environment makes the code portable across platforms. Generally, LV code can be slower than equivalent compiled C code, although the differences often lie more with program optimization than inherent execution speed.

Many libraries with a large number of functions for data acquisition, signal generation, mathematics, statistics, signal conditioning, analysis, etc., along with numerous graphical interface elements are provided in several LabVIEW package options. The number of advanced mathematic blocks for functions such as integration, filters, and other specialized capabilities usually associated with data capture from hardware sensors is immense. In addition, LabVIEW includes a text-based programming component called MathScript with additional functionality for signal processing, analysis and mathematics. MathScript can be integrated with graphical programming using "script nodes" and uses a syntax that is generally compatible with MATLAB (National 2009).

For the process this could help, calculating the important data/analysis during the run (For example the "time to temperature" or the "average temperature"). This would minimize the postprocessing time of the data. And would help for realtime presentation of the data on the web.

The LabVIEW Professional Development System allows creating stand-alone executables and the resultant executable can be distributed an unlimited number of times. The run-time engine and its libraries can be provided freely along with the executable.

There is a low cost LabVIEW Student Edition aimed at educational institutions for learning purposes. There is also an active community of LabVIEW users who communicate through several e-mail groups and Internet forums (National 2009).

5.2 Method

Figure 20 is the control software front panel programmed in LabVIEW. It is called a virtual instrument, as it reads in pressure and adjusts the automated valve to provide constant flow.

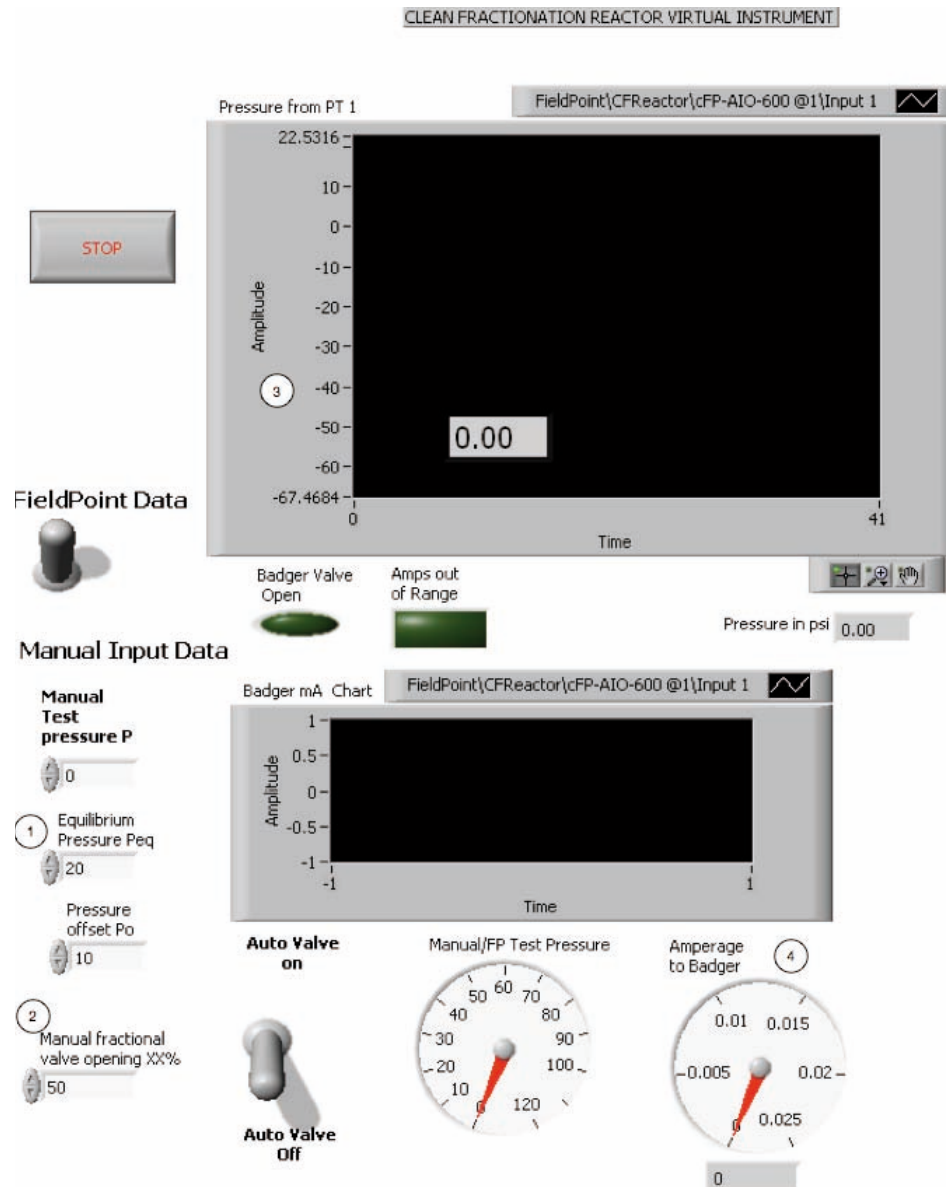


Figure 20: VI status 03-23-09

There is an entry for equilibrium pressure (1), which is the pressure result from heating to a set value, for example, 60 psi at 140 deg C. There is also an entry for the initial valve opening (2), and pressure is shown both on this graph (3) and also on a dial. The other graph and dial (4) is for amperage sent to the automated valve. Data shown is simulated values.

The goal is simple proportional control of the automated valve using pressure as an input.

Temperatures were recorded on a log-sheet every 10 *minutes* by reading the Omega controllers for the core temperature and the switch-dial for the surface temperature. Also, settings and changes were recorded on the log-sheet.

The system had very big problems with pressure fluctuation up to 20 psi, therefore a closer look to the program has been taken. The time delay was set to 500 ms, this results in a delayed reaction of the LabVIEW program. 500 *ms* after a measurement of the pressure transducer the Badger Valve reacted. This timing was much too long and so the time delay was set to 50 ms, which reduced the fluctuations to half.

The next step was reducing the amount of hand documentation. All thermocouples used (Type J) have a 2nd connection for a thermocouple wire. These connections have been used to connect the thermocouples to the FieldPoint system and finally to the LabView "write to spreadsheet" file.

Both reactors (big and small) were wired up to read, display and write the temperature profile of the core and the skin every 1 s. 1 s has been chosen to give a good profile but reduce the data to approximately 8000 data points per run. This is a maximum number of data points, which Microsoft Excel is able to handle.

5.2.1 Software

Figure 21 is the latest VI Frontpanel for the Big reactor. The difference to the small reactor is just an additional heater with a skin and core temperature measurement. The main parts of data entry and pressure graph (left side) are still the same, with little additions of setting the run temperature and run time. On the left top the entry for the flow measurements find place. The measurement has to be done manually and goes directly into the spreadsheet. In the center, a clock for the manual documentation and a timer find place. The default setting of the timer is 56 *min*, which is the time of flow, but can be changed by entering a different time. After pushing the start button, the timer also indicates that the flow is ON. This is important for the calculations in the spreadsheet. Also the display of the manual

BadgerValve has been changed. In the earlier version of the VI, this display showed the ValveOpening in mA. Now the mA are converted to the BadgerValve opening in percent. The most important addition was the temperature reading of all thermocouples. The system reads the data, display them and finally write them into an Excel spreadsheet. There is also an alarm included, if the skin-thermocouple reads a temperature higher than a specific temperature (default 400°C) or the connection has an error, an alarm goes on (flashing light and sound). There is also an indicator light when the set Run-temperature has been reached. A further addition is in the right bottom corner. This graph displays the pressure over the complete run, whereas the graph in the middle displays a time frame of 60 seconds.

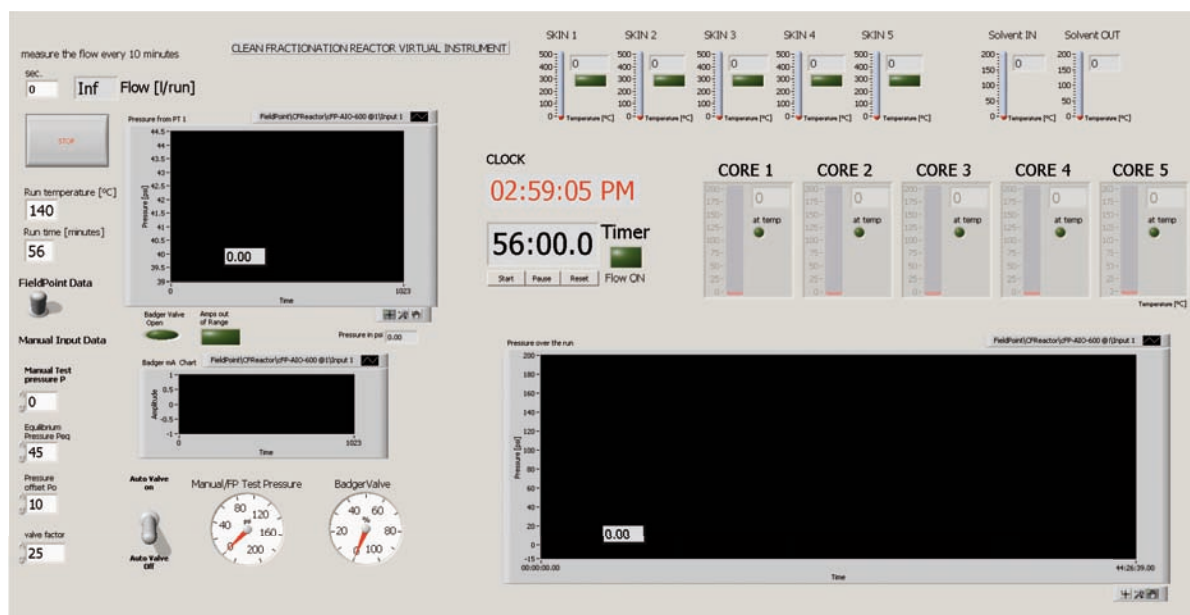


Figure 21: Front-Panel VI big reactor (07-15-09)

The programming of LabView is quiet easy, however a few training lessons (see (Bitter, Mohiuddin et al. 2001) where necessary to get a feeling for this type of programming. Behind this front-panel there is the block-diagram. The following section explains the most important parts in the block-diagram of the reactor VI. Because of the complexity of the block-diagram, the key parts have been explained here.

5.2.1.1 Simulation VI

For testing the settings and trying new steps in the VI code a simulation VI has been developed. This simulation VI does not have a FieldPoint connection; the pressure signal is simulated as a saw tooth signal with the same behavior like the PT. The simulation mode helps to understand and test how the system reacts on different settings and was also useful to determine the sample rate for writing to the spreadsheet.

5.2.1.2 Input

In the following Figure 22 the input case is shown. This is a true or false case box, if the Boolean switch on the left (FieldPoint Data) is on (true) the displayed action will be started. In the false case a manual input for testing the software gets activated. In the case structure there is on the left the CLOCK, which reads out the computer time and displays this time on the front-panel. The blue box is an EXPRESS VI for the FieldPoint input (see 5.2.3), which reads out the data of the Pressure Transducer and send the data in the blue wire (Bitter, Mohiuddin et al. 2001) to the next section. There is also an Error handler, if there is a problem with the connection or the data of the Pressure Transducer a “Continue/stop” warning “ERROR at PressureTransducer” will be displayed and the message will be recorded at the spreadsheet.

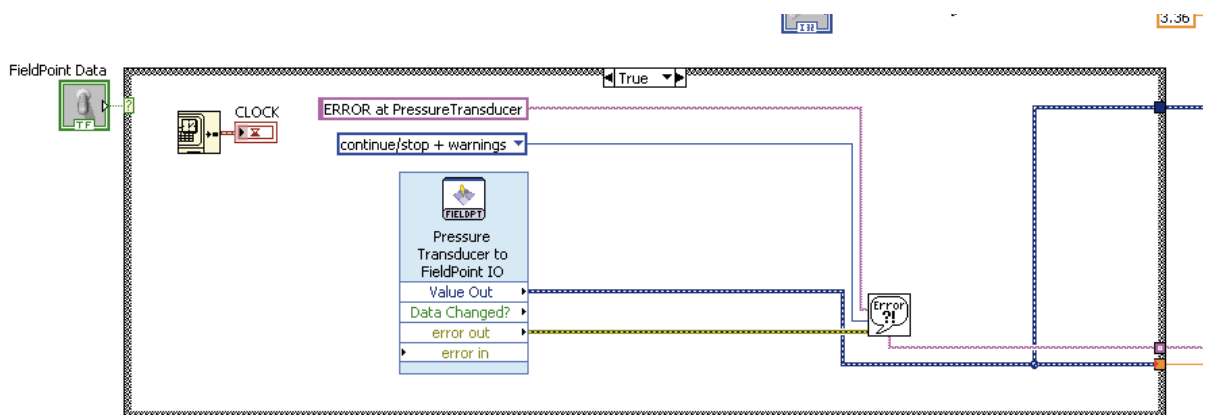


Figure 22: Input case in blockdiagram of reactor VI

5.2.1.3 Bozell or AutoValve Mode

The key part of the system is the control of the Badger Valve. There are 2 modes to choose, the first one on the left is the BozellMode and the right one is the AutoValve mode. They are pretty similar; the only difference is the condition for the true case.

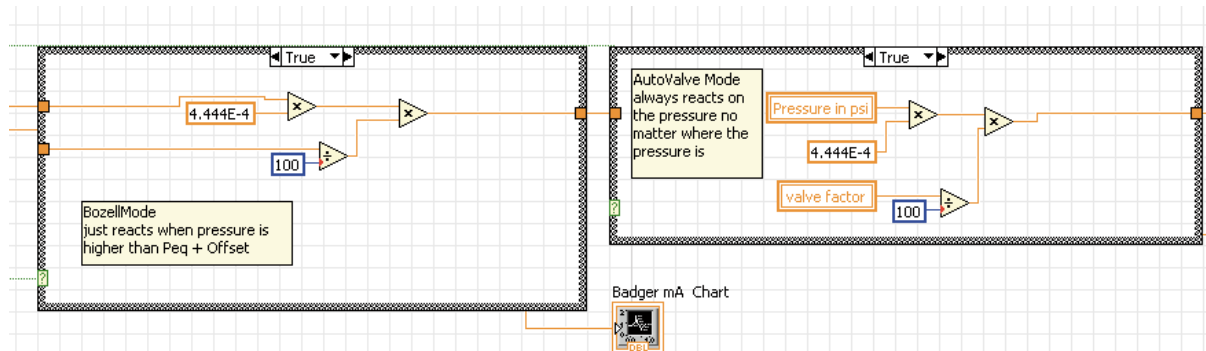


Figure 23:Bozell and AutoValve

The BozellMode gets into the true case, if

$$P_{eq} + Offset \geq PT_{pressurereading}$$

else the Valve is completely closed.

The AutoValveMode is always in the true case when it is switched on, so the Valve never close completely when the pressure is higher than zero.

The BozellMode is used for the starting sequence where the pressure in the reactor is very unstable, as soon as the pressure stabilizes, the mode can be switched to AutoValve.

5.2.1.4 Temperature

After the TC (thermocouples) have been installed to the FieldPoint Modules and updated in MAX (Measurement and Automation Explorer) they can be easily integrated into LabView. The main part is the FieldPoint Reading VI (symbol with glasses) which has different connectors (see Figure 24). On the left side there is the input where a browser window can be opened to select the correct channel.

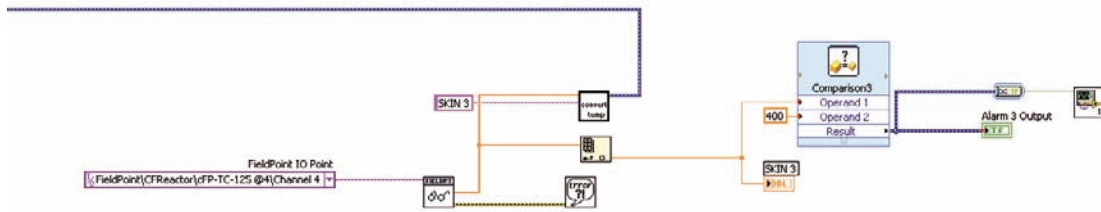


Figure 24: Skin temperature reading

On the right side of the symbol is the outlet, which has again an ERROR handler for recording and an orange data wire for transferring the data. This wire goes to a ConvertTemp VI, which adds a chosen name and converts the data to dynamic for the spreadsheet file. There is an additional comparison, if the sensor temperature is higher than the set temperature (in this case 400 °C) or the thermocouple is disconnected, in which case an Alarm VI (see 0) will be started. This alarm plays a sound file and turns the green light into a red one.

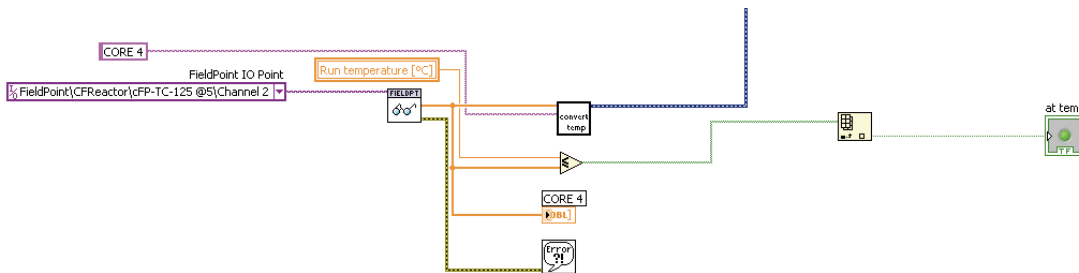


Figure 25: core temperature reading

In Figure 25 the same thing is shown for the core temperature. The only difference is that there is no Alarm VI at the end of the comparison. The comparison just indicates that the core temperature is at the set run temperature and the pump can be started.

5.2.1.5 Timer VI

The timer.vi has been downloaded from the NI forum and implemented into the existing code. The only modification was an additional indicator for “FLOW ON”. As soon as the start button is pushed the case is true and the Flow ON is lightning,

when the set time is over the light turns of. This data also goes into the spreadsheet, and is indicated as 0 for off and 1 for on in the file (Yang 2006)

5.2.1.6 Data collection

Because of the problems with pressure fluctuations, the time delay of the VI has been set to 50 ms. This leads to an large amount of data per second. To reduce the data and aquire every 1 sec. (enough to get a good resolution), this case structure has been created.

The true condition for this case is :

$$if(((i/20) - 1) * 20) = 0) _then_TRUE$$

This takes every 20th iteration of the while loop and gives, for a time delay of 50 ms, a data collection of every 1 sec.

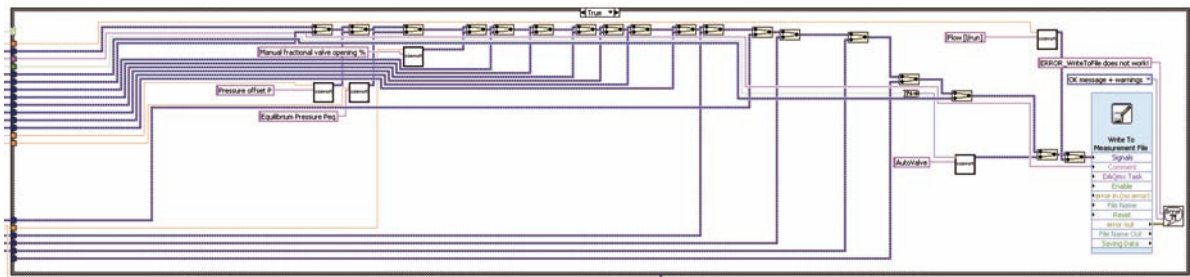


Figure 26: case structure for datacollection/reduction

In Figure 26, all the collected dynamic data wires are collected and merged. This is also the order that is used in the excel spreadsheet. On the right side there is the express VI for writing to the file. In the properties of this express file, the storage type and folder can be set.

5.2.2 Wiring

The wiring of the circuit box on the big reactor was a scale up of the small reactor. The wiring plan of the small reactor has been updated in AutoCad 2009, with the additional 5th heater band and the associated controller and relay (see APPENDIX).

To ensure that the controllers and relays are working a dry reactor test has been carried out. After this test, the thermocouples of the small and the big reactor have

been connected to the FieldPoint modules. Also, the pressure transducer of the big reactor has been connected to the FieldPoint system.

5.2.2.1 TC wiring

The thermocouples that has been used is Type J by Omega Inc. The function of a thermocouple is based on the Seebeck effect. Two different metals generate an output voltage at the connection point, this output voltage is linear to the temperature.

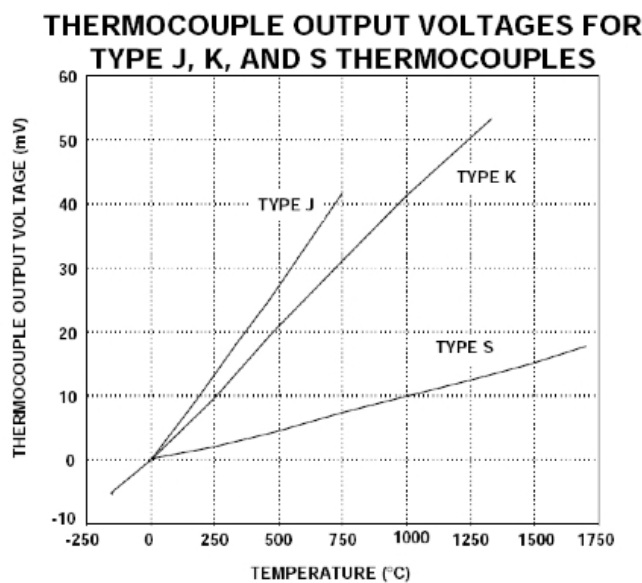


Figure 27: thermocouple output voltages for Type J, K and S thermocouples (FH-Pforzheim 2008)

In the case of a Type J thermocouple, the junction materials are Iron and Constantan. The typical temperature range is 0 to 760 °C, which fits best for the reactor measurements between 20 and 160 °C. The thermocouples used have 2 outlets to connect the wire, the first one was used to send the signal to the OMEGA controllers for controlling the temperature and the second outlet was used to send the signal to the FieldPoint IO module to monitor and record the temperature. This is also a step for a future temperature control system by LabView.

5.2.2.2 Pressure transducer

The used PT (PX319-300GI) is a stainless steel pressure transducer with a 4 to 20 mA Output. This 4 – 20 mA equals to a pressure range of 0-300 psi. To get a

linearization between pressures and output amperage, some measurements have to be done. By using a manual pressure gauge for comparing the data and measuring at three different levels (0, 50 and 160 *psi*) a good linearization can be done.

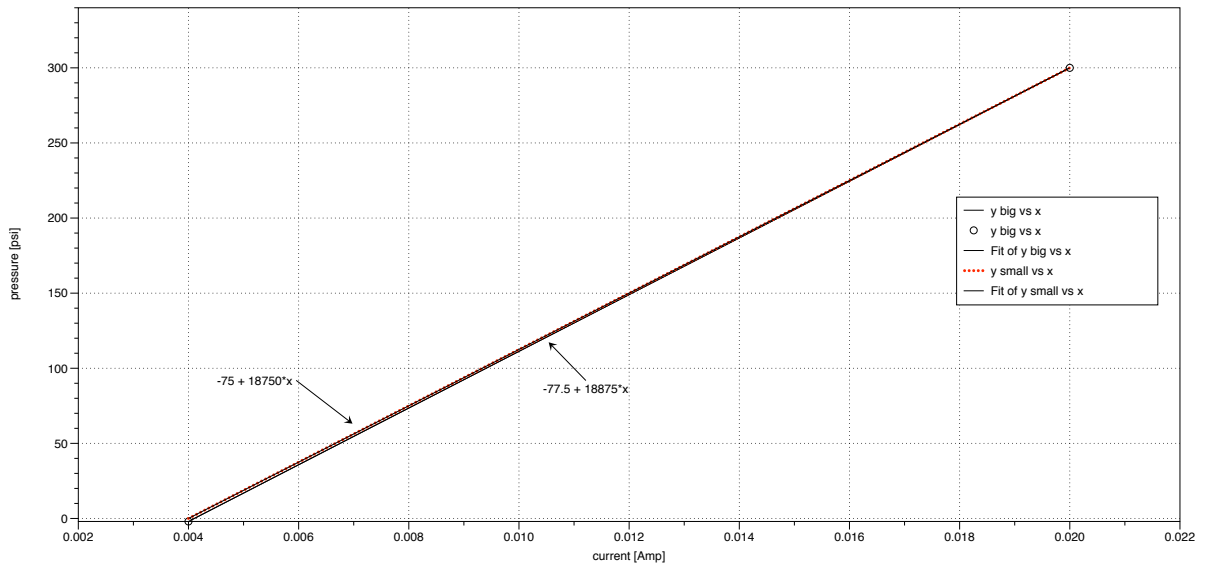


Figure 28: linearisation of the PT's

The difference between the 2 reactors is a result of the connection at the AIO module. The input of the linearization is explained in 5.2.3.

5.2.3 FieldPoint & MAX

Compact FieldPoint is an easy-to-use, highly expandable programmable automation controller (PAC) composed of rugged I/O modules and intelligent communication interfaces. The Compact FieldPoint I/O modules filter, calibrate, and scale raw sensor signals to engineering units, as well as perform self-diagnostics to look for problems, such as an open thermocouple. Through its built-in Web and file servers, the Compact FieldPoint interface automatically publishes measurements over the Ethernet network (NI Corporation 2009).



Figure 29: FieldPoint panel with the Modules

On the left side of the panel (see Figure 29) the ethernet connection find place, next to the right the first IO module is installed (cFP-AIO-600). This is a digital analog converter with 4 IN- and OUTPUTS. Here are the 2 pressure-transducers and the BadgerValve controller installed. On the next 3 slots there are the cFP-TC-125 modules installed, which take the TC's of both reactors. To calibrate and set the modules the MAX (Measurement and Automation Explorer) software is used.

5.3 Results

The LabVIEW software (VI) is at this point quiet perfect. The next step should be integration to a Database. The first steps have been completed: The Database connectivity toolkit is already installed and also the database software MS SQL Express 2005 is on the computer. The nice benefit is a fast and save data-collection, the data can be easily exported to different mathematical analyzing software (SPSS, JMP, SigmaPlot,...) and it also sets the platform for making the data public (real time data on the web).

According to the modifications on the reactor, these new elements (Flowmeter, NIR and temperature control) can be used for a PID control. A proportional–integral–derivative controller (PID controller) is a generic control loop feedback mechanism (controller) widely used in industrial control systems. A PID controller attempts to correct the error between a measured process variable and a desired setpoint by calculating and then outputting a corrective action that can adjust the process

accordingly and rapidly, to keep the error minimal. This gives the start point for a statistical process control.

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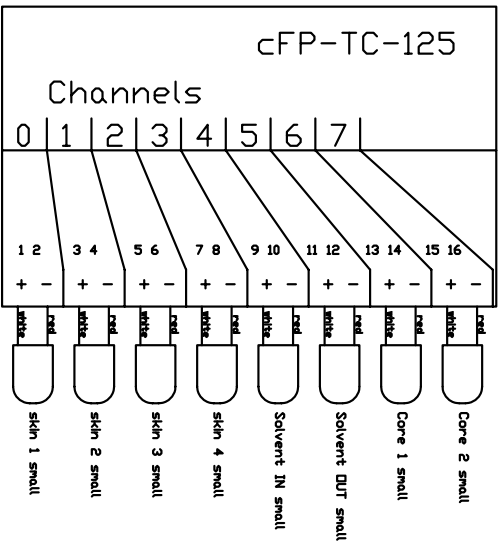
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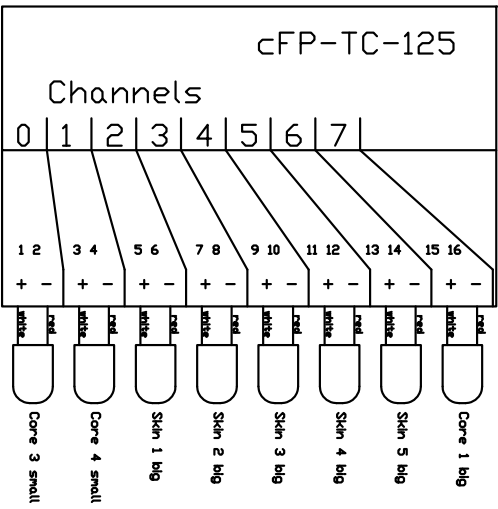
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Thermomodule 1



Thermomodule 2



Thermomodule 3

