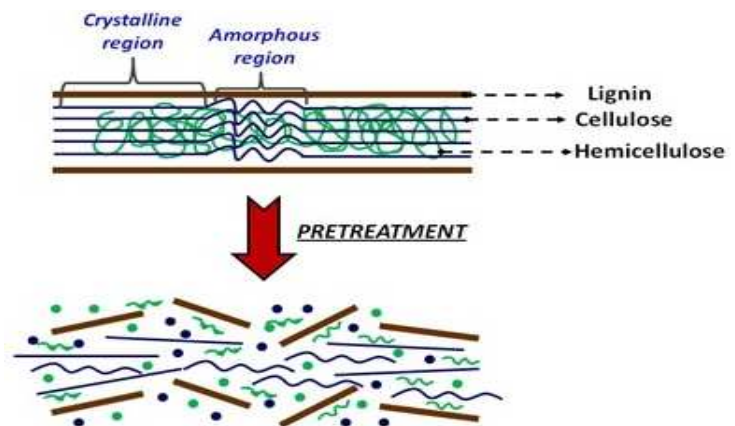


Thesis Biobased Chemistry and Technology

Process design of lignocellulosic biomass fractionation into cellulose, hemicellulose and lignin by prehydrolysis and organosolv process

Juan Holgueras Ortega

July 2015



WAGENINGEN UNIVERSITY
AGROTECHNOLOGY AND
FOOD SCIENCES

Lignocellulosic biomass fractionation into cellulose, hemicellulose and lignin by prehydrolysis and ethanol organosolv treatment

Name course : Thesis project Biobased Chemistry and
Technology
Number : 029BCT
Study load : 24 ects
Date : 15-03-2015/15-07-2015

Student : Juan Holgueras Ortega
Registration number : 900728353070
Study programme : MsC (Chemical Engineering)

Supervisor(s) : Dr. Ir. Ton Van Boxtel, Ir. Edwin Keijsers
Examiners : Dr. Elinor Scott
Group : Biobased Chemistry and Technology
Address : Bornse Weilanden 9
6708 WG Wageningen
the Netherlands
Tel:+31 (317) 48 21 24

Fax: +31 (317) 48 49 57



WAGENINGEN UNIVERSITY
AGROTECHNOLOGY AND
FOOD SCIENCES

Index

ABSTRACT	4
LIST OF FIGURES	5
LIST OF TABLES	6
1. INTRODUCTION	7
2. DESIGN OF THE PROCESS	12
3. RESULTS	18
4. DISCUSSION	23
5. CONCLUSIONS	27
6. ACKNOWLEDGEMENTS	28
7. REFERENCES	29
8. APPENDIX	32

ABSTRACT

Lignocellulosic biomass contains polymers of cellulose, hemicellulose and lignin bound together in a complex structure. The aim of this research is to find an optimized pretreatment to extract the three main components at the same time using separation steps that don't degrade any of the products during the process. A way to avoid the degradation of hemicellulose during the organosolv process with EtOH/water mixture is doing a prehydrolysis before, where the hemicellulose is dissolved in the water and then it is not submitted to the conditions of delignification during the organosolv process. The process was modelled using SuperPro Designer and, on the contrary to other processes, it included the downstream process where the products were treated with drum drying and decanters to obtain as purified as possible the products. The results obtained are very promising and show high yields for cellulose, hemicellulose and lignin of 80.3%, 54% and 60% respectively, but it has to be taken into account that there were some assumptions along the process because the data used was taken from batch processes and not for continuous processes, to reach more accurate results more experiments should be done in the lab in continuous process. Some experiments have been done in previous works where it was only studied the reactions where the components were extracted without taking into account the downstream process, which means that the products are not separated from the rest of the components and then there are no losses during the process as in this study.

LIST OF FIGURES

Figure 1. Functional block diagram of experiments done in [2] for fractionation of lignocellulose.

Figure 2. Functional flow diagram of process shown in [2] for fractionation of lignocellulose.

Figure 3. Block diagram of lignocellulosic biomass pretreatment (prehydrolysis followed by organosolv process).

Figure 4. Fraction of lignin dissolved depending on the organic solvent proportion.

Figure 5. Flowsheet of the fractionation of lignocellulose through prehydrolysis and organosolv process.

LIST OF TABLES

Table 1. Value of kinetics for reactions during the prehydrolysis step.

Table 2. Value of kinetics for reactions during organosolv process.

Table 3. Results obtained in the product stream of xylose.

Table 4. Results obtained in the product stream of cellulose.

Table 5. Results obtained in the product stream of lignin.

Table 6. Amount of chemicals used every year during the extraction process.

Table 7. Annual cost of chemicals used during the extraction process.

Table 8. Power demand in the process.

Table 9. Cost of raw materials per kg used during the process.

Table 10. Executive summary and profitability analysis of extraction process.

Table 11. Data for hydrolysis of three main components of hemicellulose in prehydrolysis and organosolv process.

Table 12. Energy recovery of the process for operations requiring cooling (Heat sources)

Table 13. Data for recirculation from first flash system (P-7 / V-101) with water stream S-147 (Outlet stream, S-105).

Table 14. Data for recirculation streams from second flash system (P-16 / V-105) and distillation columns (P-21 / C-101) and (P-23 / C-102)

Table 15. Data for recirculation streams used in the process.

Table 16. Economical evaluation of the process.

1. INTRODUCTION

High worldwide demand for energy for the production of transportation fuels, chemicals and concern over global climate change have led to an increasing interest in the development of alternative energy and chemicals that can displace fossil transportation fuel [3] [4].

Lignocellulosic materials are one of the most promising feedstock as natural and renewable resource that can be used in biorefinery. A considerable amount of such materials as waste by-products are being generated through agricultural practices mainly from various agro based industries. Recently lignocellulosic biomass have gained increasing research interests and special importance because of their renewable nature. The huge amounts of lignocellulosic biomass can potentially be converted into different high value products including bio-fuels, value added fine chemicals, and cheap energy sources for microbial fermentation and enzyme production compare to mineral fuels that are fractionated to obtain different products [5]. It represents a real alternative source of sugars (to replace starch and sugar agro feedstock), it has high availability/limited competition with food production and low-cost feedstock [6].

Apart from the three basic chemical compounds lignocellulose contains, water and minor amounts of proteins, minerals and other components. These components do not participate significantly in forming the structure of the material. [6].To efficiently use biomass for biorefinery, it needs to be fractionated into its major constituent cellulose, hemicellulose and lignin with an average composition of 30%, 45% and 25% respectively.

Inside the lignocellulose complex, cellulose retains the crystalline fibrous structure and it appears to be the core of the complex, acting as a major structural component of plant cell walls, which is responsible for mechanical strength [5]. Hemicellulose is positioned both between the micro and the macro fibrils of cellulose while lignin, which can be found in the interfibrillar area and also in the cell surface [7], provides a structural role in the matrix where cellulose and hemicellulose are embedded.

Lignin is a polymer made of three types of monomers and is amorphous (non-crystalline). It is the binder in all plants gluing the cellulose fibers together, it provides physical strength and forms the secondary wall of cells and plants [8] [9]. It is normally the most complex and smallest fraction of the biomass. It has a long-chain, heterogeneous polymer composed largely of phenyl-propane units most commonly linked by ether bonds. It is present in all plant biomass; therefore, it is considered by-product or as a residue in bio-ethanol production process [10][11].

Cellulose is more resistant and therefore requires more rigorous treatment, has a long chain of one type of beads (polymer of glucose), it forms crystals and it has the same chemical structure in every plant, it is a linear polymeric material consisting of glucose monomers connected by β -(1-4)-glycosidic linkages, leading to a fibrous and crystalline structure [12] while hemicellulose has long branched sugar chains, amorphous and it has C6, C5 and C4 sugars [9].

Unlike cellulose which is homogeneous polysaccharide, hemicellulose is heterogeneous polysaccharides composed of polymer of pentoses (xylose and arabinose), hexoses (glucose, galactose and mannose). Xylan is the main component of hemicellulose in grasses and hardwood, while glucomannan is the dominant hemicellulose component in softwood [12].

Cellulose pulp can be used for paper production or as carbohydrate source for chemicals or biofuels like bioethanol or bio-butanol. Hemicellulose-derived sugars can be used as a substrate for fermentation or anaerobic digestion. Alternatively, sugars derived from the hemicellulose fraction can be (thermo) chemically converted into furfural, which can be used as a solvent or resin. Lignin is a renewable source of aromatics for a range of chemicals and can be used as natural binders and adhesives or sub-bituminous coal [13] [14].

Recalcitrance and pretreatments

Biomass conversion is a considerable technique challenge because the cell wall is a heterogeneous solid composed of carbohydrate fraction tightly interlinked with a complex alkyl-aromatic fraction which makes the separation of the biomass complicated. There is an effect because of the biomass recalcitrance, which is the natural resistance of plant cell walls to microbial and enzymatic deconstruction [15] and makes the separation process have high cost.

The natural factors [16] that contribute to the recalcitrance of the biomass affect the liquid penetration and enzyme accessibility are the following ones:

- Relative amount of thick wall tissue.
- Structural heterogeneity and complexity of cell wall constituents such as microfibrils and matrix polymers.
- Complex structure of the plant cell wall

At the molecular level, the crystalline cellulose of cell-wall micro fibrils is highly resistant to chemical and biological hydrolysis because of its structure. There are glucose residues in the cellulose that forces a strong inter chain hydrogen bonding between adjacent chains in a cellulose chain and weaker hydrophobic interactions between cellulose sheets. This hydrophobic interactions makes crystalline cellulose resistant to acid hydrolysis because it contributes to a dense layer of water near the hydrated cellulose surface. The strong inter chain hydrogen-bonding net-work makes crystalline cellulose resistant to enzymatic hydrolysis while hemicellulose and amorphous cellulose are readily digestible [4].

Solutions to recalcitrance

The first step in the fractionation of lignocellulosic biomass into fuels or chemicals typically involves a biomass pretreatment step, which aims at making the cellulose more easily hydrolyzed by removing the hemicellulose, increasing the surface area and porosity but reducing the crystallinity of the cellulose [11] . Pretreatment is a crucial process step for the biochemical conversion of lignocellulosic biomass into bioethanol. It is required to alter the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars [17].

Pretreatment is still one of the most expensive stages within lignocellulosic biomass conversion process and there are a large number of possibilities. Minimizing energy, chemical and water inputs, preserving cellulose and hemicellulose fractions, avoiding size reduction and limiting formation of inhibitors are key issues to develop cost-effective pretreatment methods [12]. The most important pretreatments can be seen as follows:

- Mechanical Pretreatment

The reduction of particle size is essential for the fractionation to make material handling easier and to increase surface/volume ratio. This can be done by chipping, milling or grinding [18]. It can also be done using the method of ultrasonication which is a well-known technique for treatment of sludge from waste water treatment plants [19]

- Chemical Pretreatment

o *Liquid hot water (LHW)*

The biomass is treated with water at high temperature and pressure [7]. Polysaccharide hydrolysis, can result in the formation of monomeric sugars that may further decompose to furfural [20]

o *Acid hydrolysis*

Dilute (mostly sulfuric) acid is sprayed onto the raw material and the mixture is held at 160-220°C for short periods up to a few minutes [9]. The hydrolysis of hemicellulose releases monomeric sugars and soluble oligomers from the cell wall matrix into the hydrolysate. Process with a good performance in terms of recovering hemicellulose sugars but there are also some drawbacks, but acids can be corrosive and neutralization results in the formation of solid waste. This method is good for biomass with low lignin content, as almost no lignin is removed from the biomass [7].

o *Alkaline hydrolysis*

It is based on saponification of intermolecular ester bonds crosslinking xylan hemicelluloses and other compounds such as lignin [7]. It can be done with calcium or sodium hydroxide, where the addition of air or oxygen to the reaction mixture greatly improves the delignification, especially highly lignified materials [21]. The hydrolysis can also be done with ammonia (AFEX) at elevated temperatures, reducing lignin content and removing some hemicellulose while decrystallising cellulose.

o *Organosolv process*

These processes use an organic solvent or mixtures of organic solvents with water like methanol, ethanol or acetone for removal of lignin before enzymatic hydrolysis of the fraction. In addition to lignin removal, hemicellulose hydrolysis occurs leading to improved enzymatic digestibility of the cellulose fraction [7].

- *Steam explosion*

It is one of the most applied pretreatments because of its low use of chemicals and limited energy consumption. In this method high-pressure saturated steam is injected into a batch or continuous reactor filled with biomass. The temperature rises to 160-260°C, pressure is suddenly reduced and the biomass undergoes an explosive decompression with hemicellulose degradation and lignin matrix disruption as [7] [22].

- *Ionic liquid pretreatment*

Ionic liquids are a mixture of salts that melt at low temperature. Potential advantages over the methods are the ability of certain ionic liquids to dissolve/decrystallise cellulose (dissolution process) and/or to extract and dissolve lignin. Recent studies have shown that these novel solvents possess interesting properties over molecular organic solvent, such as a negligible vapor pressure, high conductivity and thermal stability, high conductivity and thermal stability, high solvating capacity for either polar or nonpolar compounds [23]. Unfortunately, the recovery of the ionic liquid is still not fully studied and the costs of the material can be a handicap.

Due to the tight structure of these three polymers, it is very difficult to convert them into biochemicals and biofuels, most recent researches have focused on the fermentation of cellulose and hemicellulose because of its content in sugars, which can be further converted into ethanol or butanol and lignin, which can be converted to added value products [7]

However, these researches focus either on the fermentation of cellulose and hemicellulose [7]. The fermentation of glucose, main product of both of them, to ethanol is an already established and efficient technique [29]. The or extraction of lignin but not on an optimized pretreatment taking into account the obtaining of the three main components at the same time.

The main question is then: Is it possible to use a pretreatment that can do a fractionation of lignocellulose that benefits the three main components?

Following the main question, the research information on processing lignocellulosic feedstock is mainly laboratory work on batch process scale. How is it possible to translate this knowledge into a large scale continuous process?

The process will be designed using SuperProDesigner and the approach is to develop a program and to evaluate the performance in order to develop an efficient separation system.

The fractionation will be performed using a two-stage separation process based on a prehydrolysis step with a weak acid dilution (H_2SO_4 + water) where the hemicellulose will be dissolved in water, followed by an organosolv process with ethanol as solvent and , where cellulose remains in the solid phase while lignin is dissolved. A possible approach to avoid degradation reactions of hemicellulose sugars is prehydrolysis of the hemicellulose fraction, this way the hemicellulose fraction does not have to be exposed to the relatively severe process conditions required for delignification. The resulting solid residue from the aqueous treatment consists mainly of lignin and cellulose and contains less inorganic and organic

extractives compared to the starting material. As a consequence, this lignin-cellulose residue seems a better feed-stock for the production of pure lignin and cellulose by organosolv delignification than the raw biomass [24].

In comparison with Kraft pulping which is the predominant chemical pulping technology, organosolv pulping has significant economic and environmental advantages. The emission of reduced sulfur as formed in Kraft pulping can be eliminated. Recovery of ethanol and dissolved lignin can be carried out with a distillation system and a precipitation system, resulting in a substantial saving in capital cost for a Kraft recovery system [2]. The extraction of lignin and recovery of ethanol can be done in the same step, without requiring another stage of separation for the ethanol recovery which doesn't happen in the Kraft pulping process.

2. DESIGN OF THE PROCESS

A prehydrolysis step followed by an organosolv process has been modelled based on the experimental data given by Ir. Edwin Keijzers and values found in the literature. The process has been modelled using the simulation program SuperPro Designer as a continuous process. The kinetics of the reaction were unknown for the continuous process, so they were set taking into account the reaction equations and separation values according to the results obtained in the experimental work done by the FBR group.

The process has been designed taken into account several sources from literature [1] [2], where it was researched the use of a prehydrolysis step before the organosolv process. However, there are some differences in the main separation steps and in the downstream process of the extraction of the products.

As it can be seen in [2], the fractionation is based on a process with two separation steps: a prehydrolysis at different temperatures from 160°C to 190°C and different concentrations of sulfuric acid that works as a catalyst in the hydrolysis of the hemicellulose and an organosolv process with temperatures from 190°C to 220°C and an ethanol/water ratio of 60/40% w/w, after each one of the processes, there is a centrifugation step where the solids are removed from the liquid stream. The lignin extraction it then treated again with another mixture of ethanol/water at the same ratio, in order to remove the lignin already dissolved that was still present after the centrifugation, and finally treated with a stream cold water 3:1 w/w in order to reduce the solvent content and precipitate the lignin.

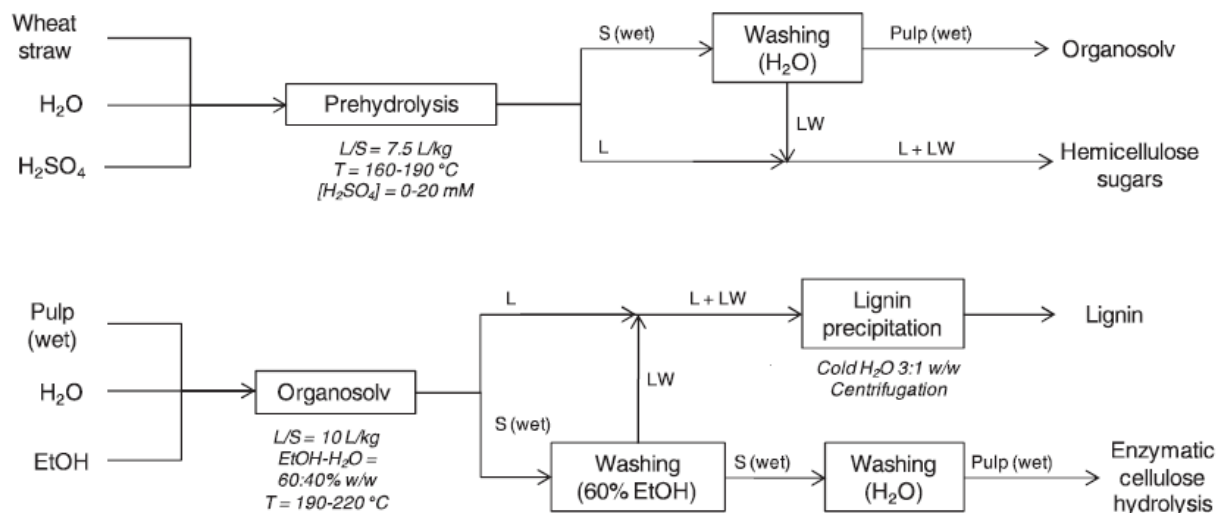


Figure 1. Functional block diagram of experiments done in [2] for fractionation of lignocellulose.

In the process explained in [1] that can be seen in Figure 2, the process is also based in the same two separation stages as before in [2]. The main differences are that this process is more based on the pH of the process to do the separation steps. The prehydrolysis is done this time with steam instead of water + H₂SO₄, as in the process mentioned before. There is no presence of sulfuric acid as catalyst in this first separation, however, it is used later after the prehydrolysis, to reduce it to a pH of 2 by adding 20% sulfuric acid at room temperature, which led to lignin precipitation that was still present after the hydrolysis of hemicellulose.

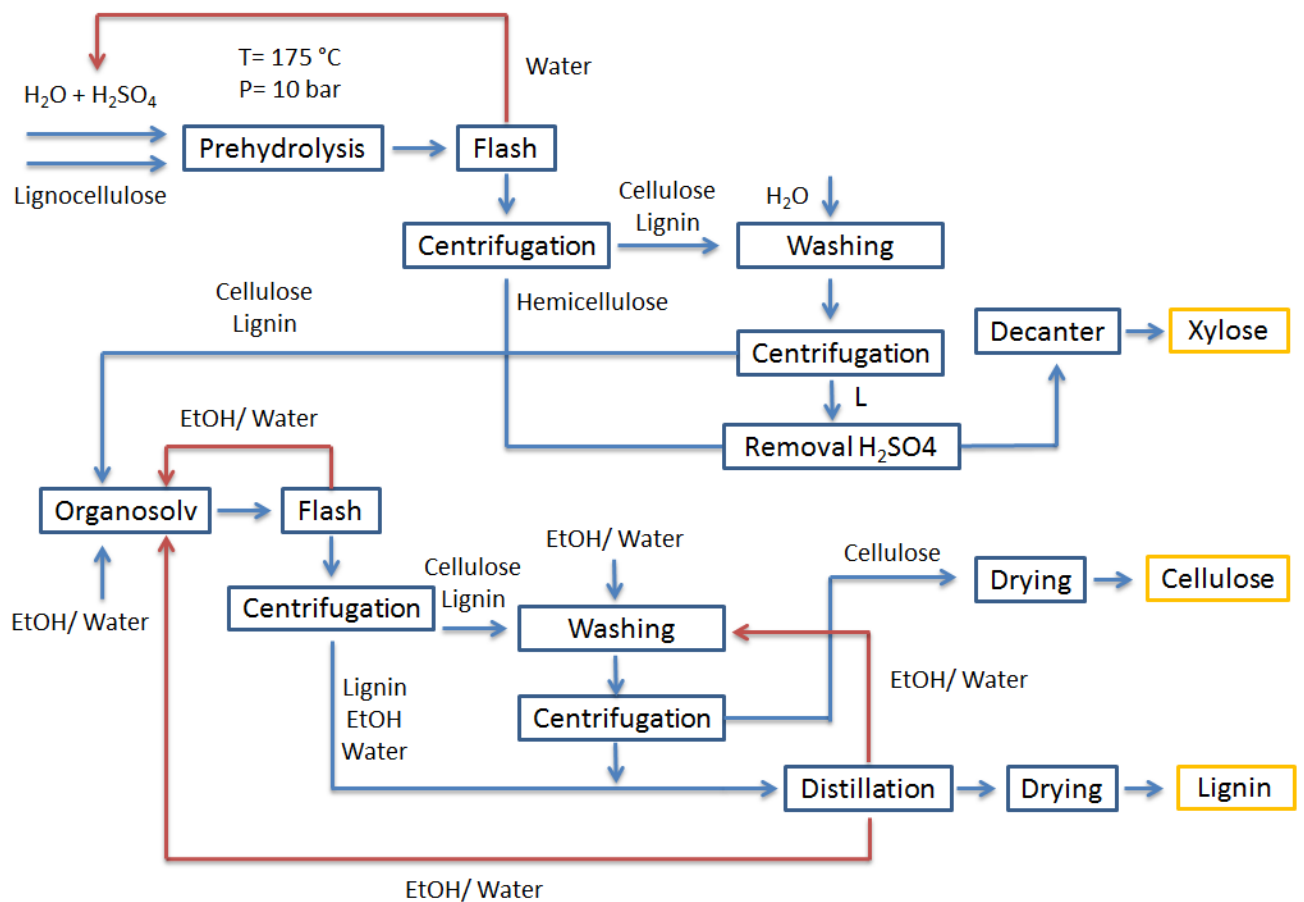


Figure 3. Block diagram of lignocellulosic biomass pretreatment (prehydrolysis followed by organosolv process).

There were some assumptions that had to be done during the process:

- The experimental data used for the prehydrolysis and organosolv process during the steps was given by Ir. Edwin Keijsers based on experiments done in FBR department and also from some experimental data from [2] (See chapter 4, Table 11). It wasn't taken into account the degradation of the glucose (cellulose and hemicellulose) and arabinose that forms hemicellulose.
- The efficiency of the centrifugation step wasn't known, the calculations were based on the hypothesis that after each centrifugation step, there should be at least 1/3 part of outlet stream in solid phase.
- In this study the hemicellulose that is dissolved in the process is referred as xylose. This is not completely accurate as the hemicellulose also contains arabinose and other compounds. The data for the other components could not be found so it was assumed that all the hemicellulose present in the process was in form of xylose

In the prehydrolysis the lignocellulose is suspended in the acidified water (20 mM), which is sprayed onto the raw material and then held at temperatures between 175°C and pressure of 10 bar with a liquid-to-solid (L/S) ratio of 7.5 L/kg dry biomass [2]. A substantial part of the xylose reacts further to furfural and degradation products like humins and lignin-furfural condensates and when the temperature is above 175°C the formation of these by-products is too high, so the temperature chosen is 175°C, when the maximum yield of monomeric and

oligomeric xylose (44% in total) is obtained [2]. The mixture is heated with high pressure steam. The hydrolysis of hemicellulose occurs, releasing monomeric sugars and soluble oligomers from the cell wall matrix into the hydrolysate. The use of a prehydrolysis step prior to organosolv delignification was found to improve the yield of xylose (hemicellulose dissolved) and the enzymatic cellulose digestibility [24]. The hemicellulose removal increases porosity and improves enzymatic digestibility, with maximum enzymatic digestibility usually coinciding with complete hemicellulose removal [7]. The stream is then taken to a flash system to remove water, which can be also recycled to the feed stream of water and as it is in vapor phase at 100 °C, it can also be used to heat the mixture of water and sulfuric acid before the prehydrolysis step. Then, there is a centrifugation to separate the solid from the liquid phase containing the hemicellulose dissolved, and another washing with water to make sure that the hemicellulose dissolved that hasn't been able to be separated in the previous centrifugation is now removed.

To remove the sulfuric acid that was used in the prehydrolysis as a catalyst, $\text{Ca}(\text{OH})_2$ was used for precipitation as $\text{Ca}(\text{SO}_4)$ and then through decanter separation from the stream containing the xylose (hemicellulose dissolved). This way, we make sure the sulfuric acid is not present during the extraction of hemicellulose, and also is a safety issue in case there is some problem of accumulation of the acid during the process, it can be well corrected by the use of this equipment.

All the reactions that take place in this step are of first order, the equations are as follows and the values of the kinetics are expressed in Table 1:



Table 1. Value of kinetics for reactions during the prehydrolysis step.

Rate reaction (min^{-1})	Value
k_1	3.0 E-02
k_2	3.6 E-03
k_3	4.3 E-04

The values of the rate reaction kinetics shown in Table 1, have been calculated taken into account the data from [2], where it is specified the amount of each component that is hydrolyzed during the reaction (for more information about the reaction in prehydrolysis see Appendix).

The pulp resulting from the prehydrolysis step is further processed with an ethanol–water ratio of 55:45% w/w to obtain a slurry with L/S ratio of 10 L solvent/kg biomass [2]. Apparently the lignin becomes more stable due to the aqueous pretreatment and is therefore harder to extract during the organosolv step, also the removal of the salts during prehydrolysis may play a role in reduction of organosolv delignification since salts have been reported to

catalyze organosolv pulping. To compensate for this reduction in the delignification, the process temperature of the organosolv fractionation step has been increased to over 175°C [2].

A higher organosolv reaction temperature improves both the delignification, the hydrolysis of residual xylan and the enzymatic digestibility of the resulting pulp. When the temperature reaches 220°C, the lignin efficiency is lower, possibly because the high temperature applied causes formation of smaller lignin fragments, which are more difficult to precipitate from the organosolv liquor upon water addition [24]. At a temperature of 200°C the delignification is high and the formation of these small fragments is minimum [24]. After the organosolv process, there is another flash system that is used to remove water and ethanol, that can be recirculated to the organosolv process keeping the same weight fraction. Following the centrifugation, there is another washing step similar to the one used in the prehydrolysis, but this time using a mixture of ethanol/water 55:45% w/w to remove the lignin dissolved that couldn't be separated in the centrifugation step. The reason why the ratio of ethanol/water is different from previous experiments [1] [2] is because of some issues with the simulation program, where it was not possible to a good distillation for the recovery, so it was chosen a lower ratio according to Figure 4, where it can be seen that the extraction also works. After the centrifugation steps ethanol and water are recovered by distillation and as then lignin precipitation is carried out. As the proportion of the organic solvent decreases, in this case ethanol, the solubility of lignin in the mixture is reduced and then the precipitation takes place. Figure 4, shows the amount of lignin dissolved depending on the ethanol/water ratio used in the several experiments, which supports the theory that when the ethanol is removed from the system the lignin present precipitates and is dissolved in the mixture [27]

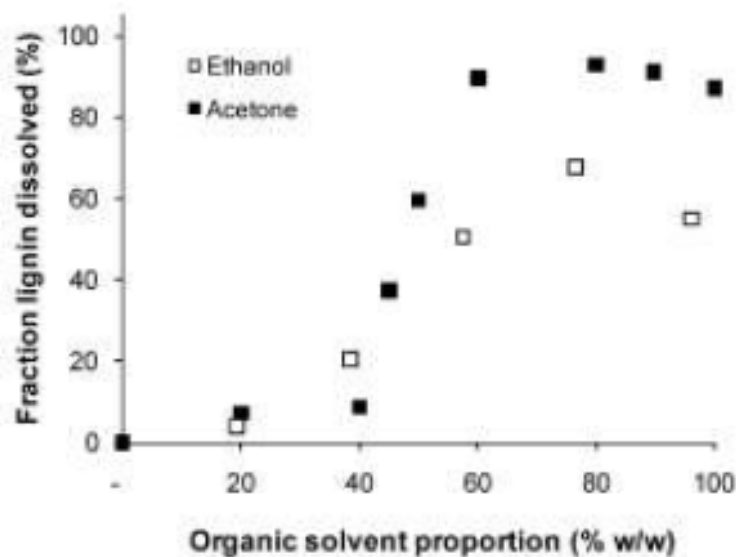


Figure 4. Fraction of lignin dissolved depending on the organic solvent proportion.

The reactions that take place during the organosolv process are like in the previous step of first order:



Hemicellulose + water → *Xylose*

(6)

Table 2. Value of kinetics for reactions during organosolv process.

Rate reaction (min⁻¹)	Value
k₁	3.8 E-02
k₂	5.2 E-04
k₃	8.7 E-03

A summary of all the equipment needed during the process has been done, with all the information required during the simulation. It can be seen in the chapter APPENDIX.

3. RESULTS

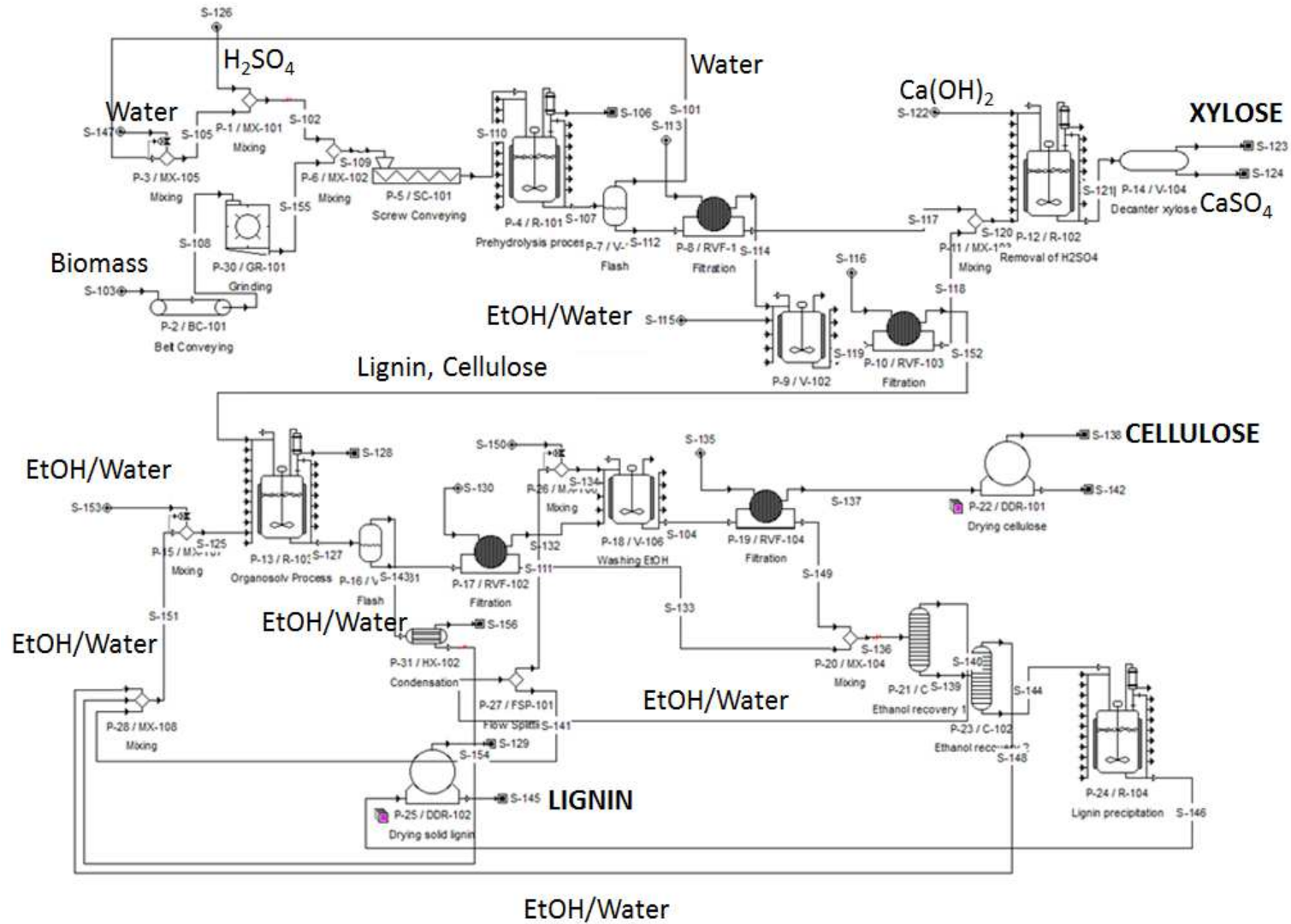


Figure 5. Flowsheet of the fractionation of lignocellulose through prehydrolysis and organosolv process.

The experimental values were based on experimental data from literature [24] and experimental values given by Ir. Edwin Keijsers from FBR group and didn't change when the process was up scaled to 10,000 T/year. The sources for experimental data was based on batch processes and they were assumed the same for continuous process developed in this study.

In chapter 2, the process was separated in two main parts: prehydrolysis and organosolv process. The process model obtained from the simulation of the process using SuperPro Designer is showed in this chapter in Figure 5.

After prehydrolysis, the centrifugation divides the stream into one based on the solid phase containing mostly cellulose, lignin and hemicellulose that hasn't been dissolved in the previous reaction and the liquid phase containing water, furfural and hemicellulose dissolved (xylose).

The results obtained for the extraction of hemicellulose in S-123 are expressed in Table 2 as follows:

Table 3. Results obtained in the product stream of xylose.

	Flowrate (kg/h)	Mass composition (%)
Water	8,880.37	97.84
Xylose	154.75	1.70
Furfural	30.82	0.34
Dissolved lignin	10.97	0.12

The yield obtained in the process for the hydrolysis of hemicellulose reaches 54%.

After the organosolv process, most lignin is dissolved in the water and cellulose remains almost intact in the solid phase. The results for the extraction of cellulose after drying in S-142 are expressed in Table 3 as follows:

Table 4. Results obtained in the product stream of cellulose.

	Flowrate (kg/h)	Mass composition (%)
Cellulose	412.25	79.81
Lignin	56.57	10.95
Hemicellulose	26.80	5.19
Ethanol	9.90	1.92
Water	8.26	1.60
Dissolved lignin	1.88	0.36
Xylose	0.83	0.16
Dissolved cellulose	0.02	4.5E-03

The yield obtained in the process for the extraction of cellulose reaches 80.25%.

Once the ethanol has been recovered, the lignin that had been dissolved previously in the organosolv process precipitates and it can be dried and extracted. The results for the extraction of lignin after drying in S-145 are expressed in Table 4. The difference between lignin and solid lignin is that the first one is the solid part from the beginning of the process that hasn't been dissolved in water in the organosolv process and the other one is the lignin that has been dissolved and later precipitated when the ethanol was removed

Table 5. Results obtained in the product stream of lignin.

	Flowrate (kg/h)	Mass composition (%)
Solid Lignin	203.74	79.81
Cellulose	30.55	10.89
Water	14.64	5.22
Lignin	9.60	3.42
Xylose	6.50	2.32
Dissolved cellulose	4.60	1.64
Hemicellulose	4.54	1.62
Dissolved lignin	3.12	1.11
Ethanol	2.95	1.05
Furfural	0.12	0.04

The yield obtained in the process for the extraction of lignin reaches 60%.

SuperPro Designer can also give reports about economic evaluation of the process, pointing the most important factors to see if the process can be feasible or not. The reports are given automatically by the program, no calculations were made.

Table 6 gives the amount of materials used in the process and the amount of utilities used in the process.

Table 6. Amount of chemicals used every year during the extraction process.

Material	Flowrate (kg/year)
Ca Hydroxide	75,398.40
Cellulose	4,068,504.00
Ethanol	5,090,351.76
Hemicellulose	2,260,368.00
Lignin	2,712,600.00
Sulphuric Acid	99,712.80
Water	87,259,891.39
Heat transfer agent	Flowrate (kg/year)
Cooling water	9,128,317,740.28
Steam	103,464,111.15
Steam (High P)	31,169,003.97

Table 7 shows the costs associated with the materials and the utilities:

Table 7. Annual cost of chemicals used during the extraction process.

Material	Annual cost (€)
Ca Hydroxide	145,812
Cellulose	203,425
Ethanol	2,792,427
Hemicellulose	113,018
Lignin	13,563
Sulphuric Acid	5,105
Water	8,693
Total	3,404,064
Utilities	Annual cost (€)
Std Power	120,847
Steam	908,130
Steam (High P)	455,957
Cooling water	333,840
Total	1,818,774

Table 8 shows the power demand that requires the process every year and the cost :

Table 8. Power demand in the process.

Std Power	Kw-h/year
R-101 : P-4 (Hemicellulose hydrolysis)	156,511.96
BC-101 : P-2 (Belt conveying)	9,041.47
SC-101 : P-5 (Screw conveying)	28,835.11
R-103 : P-13 (Organosolv process)	180,058.47
DDR-101 : P-22 (Dryer cellulose)	21,336.64
DDR-102 : P-25 (Dryer lignin)	21,828.50
GR-101 : P-30 (Grinder)	904,147.20
Unlisted Equipment	82,609.96
General Load	247,829.88
Total	1,652,199.19
Std Power (0.10 €/Kw-h)	€/year
Total	165,219.92

The total cost of the process can be seen in Table 9, where the investment, operating and revenues cost are shown.

Table 9 shows the raw materials costs used in the process and the selling prices fixed for the main products produced:

Table 9. Cost of raw materials per kg used during the process.

Raw materials cost	€/kg	€/year
Ca Hydroxide	1.75	145,812
Cellulose	0.05	203,425
Ethyl alcohol	0.55	2,792,381
Hemicellulose	0.05	113,018
Lignin	0.05	135,630
Sulphuric acid	0.44	51,050
Water	1E-04	8,693
Total	2.89	3,450,009
Selling price products	€/kg	Revenues (€/year) (Table 10)
Cellulose	1.75	
Hemicellulose	2	
Lignin	1.5	
Furfural	1.5	

Table 10 shows a summary of the profitability analysis of extraction process:

Table 10. Executive summary and profitability analysis of extraction process.

Investment costs(€)	34,397,000
Operating costs (€/year)	5,223,000
Revenue xylose and furfural (€/year)	1,461,672
Revenue lignin (€/year)	3,106,753
Revenue cellulose (€/year)	7,421,039
Total revenue (€/year)	11,989,464
Steam savings (€/year)	252,576
Cooling water savings (€/year)	106,043
Total savings (€/year)	358,619

The operating costs don't include the data of labor-dependent, facility-dependent and laboratory/QC/QA. The operating costs shown in Table 10 were calculated as the sum of raw materials and utilities used in the process.

4. DISCUSSION

In this report there are some similarities with two processes mentioned in chapter 2 [1] [2] but there are also some differences that can be appreciated:

- The prehydrolysis step is based on the information present in [2], where the hemicellulose is dissolved in water with the presence of sulphuric acid as catalyst. The temperature chosen has been selected according to the optimal one calculated in [2], which was 175°C and p=10bar with 60% of hemicellulose hydrolysed, indeed the formation of furfural as by-product is also taken into account in the design of the process. There is a centrifugation step following the prehydrolysis and a washing step with water, where the hemicellulose that has been previously dissolved in the process and hasn't been separated in the centrifugation is removed.
- In the organosolv process, the ratio chosen is very similar to the one used in [2] where it was 60:40 % w/w, whereas in this study is 55:45% w/w due to better performance in the simulation program. The temperature and pressure were also selected according to literature [2] [26]. There is also a washing step after it with the same EtOH/water ratio.

The main differences between these last two processes shown before and our research are:

- After the prehydrolysis step, before centrifuging, a flash has been installed in order to remove some water that came from the reactor. The water that removed was in vapour state, and then could be recycled to the beginning of the process to save money in the purchase of water in feed stream (S-105) and also it was used to heat the mixture with sulphuric acid before the hydrolysis of hemicellulose to 100 °C.
- In this study, the presence of sulphuric acid that is used as catalyst is considered as a toxic compound. As it can be read in [1] its presence can be removed by adding lime ($\text{Ca}(\text{OH})_2$) and then recovered as gypsum (CaSO_4). After the washing step and centrifugation the hemicellulose dissolved is separated from the gypsum with a decanter.
- In our process, the stream containing lignin with water and ethanol is treated in several distillation towers where ethanol is removed along with water and then lignin precipitates, in this way ethanol can be easily recovered and be reused in the organosolv process and washing step. Unlike the processes developed for now using only organosolv processes without prehydrolysis [7], now it is not required such a high ethanol/water ratio to hydrolyse the lignin, which is translated into less spending on distillation processes for the recovery of ethanol. The use of distillation columns also saves the problematic using strong acids (H_2SO_4) to precipitate the lignin [1], which can be very corrosive and must be recycled to lower the cost.
- Both streams containing cellulose and lignin at the end of the process, are submitted to drum drying to remove the water present and obtain the products as purified as possible.

During the design of the process with SuperPro Designer, there were some assumptions that had to be done to develop the process. The values for the kinetics in both reactions of

hydrolysis of hemicellulose (prehydrolysis) and lignin (organosolv) were missing because for the moment, the experiments have not been done in continuous mode in experimental work in the lab.

According to some data found in literature [2] and some experiments done by FBR department in the pilot plant, following a batch process, the amount of the components that is dissolved in the processes is presented in Table 11 as follows:

Table 11. Data for hydrolysis of three main components of hemicellulose in prehydrolysis and organosolv process.

	PREHYDROLYSIS			ORGANOSOLV PROCESS		
	Lignin	Hemicellulose	Cellulose	Lignin	Hemicellulose	Cellulose
% Dissolved	5	60	-	80	50	5

Data for hydrolysis of hemicellulose in prehydrolysis from [2], the rest of data obtained from lab experiments done by FBR department

The kinetics used in both separation steps were supposed taking into account the data given in Table 15 for a batch process.

Throughout the process, high amounts of water are used to dissolve the components or do washing steps. The use of centrifugations is then really important to separate the products dissolved from the ones that remain in the solid phase. Efficiencies for centrifugation processes couldn't be found in literature, it was assumed that after each centrifugation, in the solid phase there was 1/3 of the total value of the stream in form of lignocellulose (cellulose, hemicellulose and lignin that are not hydrolyzed and remain in the solid phase in the same form as the feed stream of the process).

The process requires high amount of energy. The program could also do an energy recovery report where it was included which processes could be heated using other items on the process.

The energy recovery of the process done with the simulation process is expressed in Table 12 as follows:

Table 12. Energy recovery of the process for operations requiring cooling (Heat sources).

Operation	Cooling load (kcal/h)	T _{in} (°C)	T _{out} (°C)	Cooling agent	Recipient	Matching %
P-21: DISTILL-1	3,468,615.1	92.8	92.8	Cooling water [25°C-30°C]	P-25: DRY-1	26.7
P-23: DISTILL-1	1,157,464.7	92	92	Cooling water [25°C-30°C]	P-22: DRY-1	78.2

In the distillation columns used for the recovery of ethanol and water and therefore the precipitation of lignin, it is necessary to cool down the out streams. P-25: DRY-1, is the dryer system used for the purification of the lignin, while P-22: DRY-1, is the one used for the purification of the cellulose.

According to the report given by the simulation program, 26.7% of the heat requirements of the first distillation column can be given by P-25: DRY-1 and 78.2% for the second distillation column can be given by P-22: DRY-1.

During the process a high amount of ethanol and water is removed through the flash systems and distillation after the organosolv process where ethanol is removed so lignin can precipitate and then be extracted. In the first part of the process after the prehydrolysis, in the goal to remove water from the process it was used a flash system (P-7 / V-101), where it was removed 13% of the water in vapor phase. This stream composed entirely by water was recovered to the beginning of the process and mixed with the feed stream of water (S-147), just before mixing it with the sulfuric acid. Indeed, the high temperature of the vapor stream made the temperature of the stream that enters in the prehydrolysis step increase and then less utilities had to be used in this step. The data of this recovery can be seen in Table 13 as follows:

Table 13. Data for recirculation from first flash system (P-7 / V-101) with water stream S-147 (Outlet stream, S-105).

Add-Inn stream (kg/h)	1,111.65
Process stream (kg/h)	7,442.95
Outlet stream (kg/h)	8,554.60

After the organosolv process, there are several steps where a mixture of ethanol and water is removed: in the flash system (P-16 / V-105), first distillation column (P-21 / C-101) and second distillation column (P-23 / C-102). The feed stream (S-152) used in the organosolv process had an EtOH/water ratio (55:45 w/w %), the same as the stream that was used for the washing step in P-18 / V-106 to remove the remaining dissolved lignin. The streams coming from these equipment mentioned before, were mixed in order to get the same ratio as S-152. The data of the streams that were mixed to be recirculated can be seen in Table 14 as follows:

Table 14. Data for recirculation streams used in the process.

	S-140	S-111	S-141	S-143	S-148
Ethanol (kg/h)	4,583.55	870.87	3,712.68	1,089.1	920.77
wi	0.56	0.56	0.56	0.49	0.60
Water (kg/h)	3,633.08	690.26	2,942.8	1,130.58	618.22
wi	0.44	0.44	0.44	0.51	0.40
Total (kg/h)	8,216.63	1561.13	6,655.48	2,219.68	1,538.99

S-111 and S-141 come from the same source (S-140) that is the stream from the first distillation column (P-21 / C-101). The first one is recirculated to the washing step in P-18 / V-106 while the second one is sent to the organosolv process with the other two streams S-143 and S-148. The results for the recovery streams are shown in Table 15 as follows:

Table 15. Data for recirculation streams that are reused in the organosolv process.

	Add-In stream	Process stream	Outlet stream
Ethanol (kg/h)	5,722.58	572.81	6,295.4
wi	0.55	0.55	0.55
Water (kg/h)	4,691.59	470.4	5,161.99
wi	0.45	0.45	0.45
Total	10,414.17	1,043.21	11,457.39

With the data presented in Table 14, 91.1% of the ethanol and 37.6% of water can be recovered. It should be studied if the recovery of ethanol can be higher installing another distillation column to recover the ethanol, as in other researches [28], it is said that it can reach 95% recovery.

The economical evaluation of the process is shown in chapter 3 (Results). The most important data that can be used to see if the process can be feasible or no is shown in Table 16 as follows:

Table 16. Economical evaluation of the process.

Investment costs(€)	34,397,000
Operating costs (€/year)	5,223,000
Total revenue (€/year)	11,989,464
Total savings (€/year)	358,619

To calculate the operating costs, it wasn't taken into account the labor cost.

Comparing the results obtained from Table 16, it can be seen that the revenues obtained from selling cellulose, hemicellulose and lignin, along with the savings from heat integration, are significantly higher than the money spent in raw materials and utilities (operating costs). The labor costs were not considered because the program SuperPro gave too high default values, the same happens with CAPEX values, the equipment costs were too high, and therefore were not considered in this study.

5. CONCLUSIONS

In this work a process is proposed for the production of hemicellulose, cellulose and lignin. The process is based on conversion data from literature and data from FBR department. To obtain these three products, this study proposes to use another separation step before the organosolv process in order to avoid the degradation that hemicellulose can suffer due to the extreme conditions it works with. The previous step was based on a prehydrolysis using a mixture of water and sulfuric acid 20 mM to provoke the hydrolysis of the hemicellulose. Then, the organosolv process is applied to hydrolyze the lignin present in the process, which didn't require so high temperatures as the process without prehydrolysis. The simulation model for the fractionation of lignocellulose shows high yields for the three main components recovery with the pretreatment proposed in this study.

The high yields obtained in the simulation process supports this theory and the easy recovery of the ethanol makes the process very interesting to look into. Being the operating costs lower than the total revenue obtained from the sale of the products, it is interesting to think that a new path can be found to optimize the process to try to design a future pilot plant taking into account this time some economic data that hasn't been looked into here like the labor-dependent, facility-dependent and laboratory/QC/QA costs. This study is a first step to design a process to fractionate lignocellulose and obtain intact the three main components cellulose, hemicellulose and lignin it is formed, continuous process seems to be possible and it is a promising interesting path to investigate into, however it requires more study to optimize the process in terms of heat integration, recovery of materials and search of kinetics that can work in continuous processes.

6. ACKNOWLEDGEMENTS

I would like to thank a lot of people who have supported me not only in this last year of master thesis but also in my bachelor and in my master, and without them it couldn't have been possible.

First of all, I would like to thank prof. Dr. JH (Harry) Bitter and Dr. Van Boxtel (Ton) as head of the department and supervisor for the opportunity to work at the Chair group Biobased Chemistry & Technology (BCT) during this internship. Many thanks to Dr. M. Fdez. Polanco and Dr. R.B. Mato for making this exchange possible and give me the chance to enjoy this experience.

I am very grateful to my supervisor Dr. Van Boxtel (Ton) and Ir. Keijsers (Edwin) for all the things they have taught me during this last 4 months, in both academic and personal field.

Out of work, I would like to express my love and gratitude to my family, specially my parents Jesús and Nines, my brother Javier and my sister Elena. Thank for all your support and encouragement, for believing in me and for being there in the good moments and especially in the bad moments.

7. REFERENCES

- [1] Separation of lignocellulosic material by combined processes of prehydrolysis and ethanol extraction (2011). Zehua Liu, Pedram Fatehi, M. Sarwar Jahan, Yohghao Ni. *Bioresource Technology*, Vol.102, 1264-1269.
- [2] Fractionation of wheat straw by prehydrolysis, organosolv delignification and enzymatic hydrolysis for production of sugars and lignin (2012). W.J.J. Huijgen, A.T. Smith, P.J. de Wild, H. den Uil. *Energy Research Centre of The Netherlands (ECN)*. Vol. 114, 389-398.
- [3] High added value valorisation of lignin for optimal biorefinery of lignocellulose to energy carriers and products (2011). Richard J.A. Gosselink. *Energy Research Central of The Netherlands*.
- [4] Biomass Recalcitrance: Engineering Plants and Enzymes for Biofuels Production (2007). Michael E. Himmel, Shi-You Ding, David K. Johnson, William S. Adney, Mark R. Nimlos, John W. Brady, Thomas D. Foust. *Sustainability and Energy*, Vol. 315, 804-807.
- [5] Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: A brief review (2014). Zahid Anwar, Muhammad Gulfraz, Muhammad Irshad. *Journal of Radiation Research and Applied Science*, Vol. 7, 163-173.
- [6] Lignocellulosic biorefineries: concepts and possibilities (2014). Kennet F. Reardon. *Advances in Plant Biology*, Vol.4, 255-267.
- [7] Literature review of physical and chemical pretreatment processes for lignocellulosic biomass (2010) P.P.H Harmsen, W.J.J. Huijgen, L.M. Bermúdez López, R.C.C. Bakker.
- [8] Lignin Production by Organosolv Fractionation of Lignocellulosic Biomass (2010), Wouter Huijgen, Paul de Wild & Hans Reith, *International Biomass valorisation congress in Amsterdam, The Netherlands*.
- [9] Conversion of cellulose, hemicellulose and lignin into platform molecules: biotechnological approach. Anders Frolander (2011), *Borregaard Industries Ltd, Norway*.
- [10] Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term (2005), Carlo N. Hamelinck, Geertje van Hooijdonk, André PC Faaij. *Biomass and Bioenergy*, Vol.28, 384-410.
- [11] A roadmap for conversion of lignocellulosic biomass to chemicals and fuels (2012) , Stephanie G Wettstein, David Martin Alonso, Elif I Gürbüz and James A Dumesic, *Current Opinion in Chemical Engineering*, Vol. 1, 218-224.
- [12] Pretreatment and fractionation of lignocellulosic biomass for production of biofuel and value-added products (2012), Yoo, Chang Geun. *Graduate Theses and Dissertations*. PAPER 12700.

- [13] Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose (2013). Jelle Wildschut, Arjan T. Smith, Johannes H.Reith, Wouter J.J. Huijgen. Vol. 135, 58-66.
- [14] Biorefinery–systems (2004). Kamm B., Kamm M., Chem. *Biochem. Eng. Q.* Vol. 181 1–6.
- [15] Deconstruction of lignocellulosic biomass to fuels and chemicals, Shishir P. S. Chindawat (2011). *Annual Review of Chemical and Biomolecular Engineering*, Vol. 2, 121-145.
- [16] Lignocellulosic feedstock biorefinery for co-production of chemicals, transportation, fuels, electricity and heat (2009), J.H. Reith, R. van Ree, R. Capote Campos, R. R. Bakker, P.J. de Wild, F. Monot, B. Estrine, A.V. Bridgwater, A. Agostini, *Energy Research Centre of the Netherlands*
- [17] P. Industrial biotechnology for production of bio-based chemicals (2007). Hatti-Kal, R.Iornvall, *U. Trends Biotechnol.* Vol. 25, 119-124.
- [18] Ethanol production from wheat straw by *Saccharomyces cerevisiae* and *Scheffersomyces stipitis* co-culture in batch and continuous system (2014). Pinar Karagöz. Melek Özkan. *Bioresource Tehcnology*, Vol. 158, 286-293.
- [19] High-performance hydrolysis of cellulose using mixed cellulase species and ultrasonication pretreatment (2004). Imai, M., Ikari, K. and Suzuki, I. *Biochemical Engineering Journal*, Vol. 17, 79-83.
- [20] Features of promising technologies for pretreatment of lignocellulosic biomass (2005). Nathan Mosier, Charles Wyman, Bruce Dale, Richard Elander, Y.Y.Lee, Mark Holtzapple, Michael Ladisch. *Bioresource Technology*, Vol. 96, 673-686.
- [21] Fundamental factors affecting biomass enzymatic reactivity (2000). Vincent S. Chang, Mark T. Holtzapple. *Journal of Applied Biochemistry and Biotechnology*. Vol. 84-86, 5-37.
- [22] Hydrolysis of lignocellulosic materials for ethanol production: a review, Ye Sun, Jiayang Cheng (2002). *Bioresource Technology*, Vol. 83, 1-11.
- [23] Fractionation of lignocellulosic biomass with the ionic liquid 1-butylimidazolium hydrogen sulphate (2014), Pedro Verdía, Agnieszka Brandt, Jason P. Hallett, Michael J. Ray and Tom Welton. *Royal Society of Chemistry*, Vol. 16, 1617.
- [24] Lignin precipitation on the pulp fibers in the ethanol-based organosolv pulping (2007). Yongjian Xu, Kecheng Li, Meiyun Zhang. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol. 301, 255-263.
- [25] Extraction and characterization of hemicelluloses and cellulose from oil palm trunk and empty fruit bunch fibres (1999). Sun, R.C., Fang, J.M., Mott, L., Bolton, J. J. *Wood Chem. Technol.* Vol 19 (1-2), 167-185.

[26] Organosolv process (2012). Alex Berlin, Mikhail Y. Balakshin, Raymond Ma, Gutman Vera Maximenko, Darwin Ortiz. Publication number CA2803177 A1.

[27] Features of promising technologies for pretreatment of lignocellulosic biomass (2005). Nathan Mosier, Charles Wyman, Bruce Dale, Richard Elander, Y.Y. Lee, Mark Holtzapple, Michael Ladisch. *Bioresource Technology*, Vol. 96, 673-686.

[28] Ethanol recovery process (2010). Anurag P. Mairal, Alvin Ng, Richard W. Baker, Ivy Huang, Jennifer Ly. Publication number US7732173 B2.

[29] Direct ethanol production from hemicellulosic materials of rice straw by use of an engineered yeast strain codisplaying three types of hemicellulolytic enzymes on the surface of xylose utilizing *Saccharomyces cerevisiae* cells (2012). Sakamoto, T., Hasunuma, T, Hori, Y., Yamada, R., Kondo, A. *Journal of Biotechnology*, Vol 158, 203-210.

8. APPENDIX

Code	Type of equipment	Function	Remark
P-2 / BC-101	Belt conveying	Transport solid lignocellulose to the grinder	Convey solids, with a specific loading rate of 200000 L/m ² h
P-30 / GR-101	Grinder	Size reduction of lignocellulose to a more suitable particle size	-
P-3 / MX-105	Custom Mixing	Adjust flow of Add-In stream and mix it with the Process stream to reach an outlet stream mass flow	Outlet stream mass flow of 8554.6 kg/h
P-1 / MX-101	Mixer	Mix streams of water and sulfuric acid	-
P-6 / MX-102	Mixer	Mix streams of acidified water from mixer P-1 / MX-101 with lignocellulosic biomass from grinder	-
P-5 / SC-101	Screw conveying	Convey the slurry stream made by biomass and acidified water to the prehydrolysis process	Convey solids, with a specific throughput of 200000 L/m ² h
P-4 / R-101	Continuous Kinetic Reaction	Hydrolysis of hemicellulose and furfural as by-product. Execute reactions (1), (2), (3) at 175°C and P=10 bar with volume ratio of 90%	Out stream of the reaction: hemicellulose (60% xylose. 20% remains solid, 20% furfural) lignin (5% lignin is dissolved). The reaction used a L/S ratio of 7.5 L / kg dry biomass. Data from [2] and experimental data of FBR department.
P-7 / V-101	Phase change : Flash	Remove water of the stream from the reactor P-4 / R-101.	Flash works with a user-defined vapor/liquid split and under adiabatic conditions of 1.013bar and 100.34°C
P-8 / RVF-101	Rotary vacuum filtration	Filtrate water with hemicellulose and lignin dissolved from cellulose, hemicellulose	Filter at a flux of 250 L/m ² h, to cake porosity 0.30 v/v, wash solvent flowrate

		and lignin that is still solid	is 60.32 L/h
P-11 / MX-103	Mixer	Mix liquid streams from the centrifugations P-8 / RVF-101 and P-10 / RVF-103 (after reaction and washing step with water)	-
P-12 / R-102	Continuous Stoichiometric Reaction	Removal of sulfuric acid, making it react with $\text{Ca}(\text{OH})_2$ and then precipitate in form of CaSO_4 $\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$	Reaction works under adiabatic conditions and at 1bar
P-14 / V-104	Decanting	Separate hemicellulose dissolved in water from the precipitates CaSO_4	Decant two immiscible liquid phases, the pressure is 1.013bar
P-9 / V-102	Washing water	Do another washing step with water to remove the xylose that hasn't been filtrated before in the centrifugation P-8 / RVF-101	Washing step continuously and it works under adiabatic conditions and pressure is 1bar. The washing used a L/S ratio of 3L / kg dry biomass
P-10 / RVF-103	Rotary vacuum filtration	Filtrate solid stream that comes from P-8 / RVF-101 and separate remained hemicellulose dissolved in water from the rest	Filter at a flux of 250 $\text{L}/\text{m}^2\text{h}$, to cake porosity 0.40 v/v, wash solvent flowrate is 60.32 L/h
P-15 / MX-107	Custom mixing	Adjust flow of Add-In stream and mix it with the Process stream to reach an outlet stream mass flow	Outlet stream mass flow of 11457.38 kg/h
P-13 / R-103	Continuous Kinetic Reaction	Hydrolysis of lignin and hemicellulose that remained solid. Execute reactions (4), (5), (6) at 195°C and $P=30$ bar with volume ratio of 90%	Out stream of the reaction: hemicellulose (50% xylose) lignin (80% is dissolved), cellulose(5% dissolved). The reaction used a L/S ratio of 10L solvent (ethanol) / kg biomass. Data from [2] and experimental

			data of FBR department
P-16 / V-105	Phase change: Flash	Remove water and ethanol of the stream from the reactor P-13 / R-103	Flash works with a user-defined vapor/liquid split and under adiabatic conditions of 1.013bar and 101.4°C
P-17 / RVF-102	Rotary vacuum filtration	Filtrate water with mostly lignin dissolved and low amounts of hemicellulose and cellulose dissolved	Filter at a flux of 250 L/m ² h, to cake porosity 0.30 v/v, wash solvent flowrate is 60.32 L/h
P-26 / MX-106	Custom mixing	Adjust flow of Add-In stream and mix it with the Process stream to reach an outlet stream mass flow	Outlet stream mass flow of 1688.51 kg/h
P-18 / V-106	Washing EtOH / water 55:45	Do another washing step with EtOH / water 55:45 to remove the lignin dissolved that hasn't been filtrated before in the centrifugation	Washing step continuously and it works under adiabatic conditions and pressure is 1bar
P-19 / RVF-104	Rotary vacuum filtration	Filtrate water with mostly lignin dissolved and low amounts of hemicellulose and cellulose dissolved	Filter at a flux of 250 L/m ² h, to cake porosity 0.40 v/v, wash solvent flowrate is 60.32 L/h
P-20 / MX-104	Mixer	Mix liquid streams from the centrifugations P-17 / RVF-102 and P-19 / RVF-104 (after reaction and washing	-
P-21 / C-101	Distillation continuous column	Do the recovery of the ethanol/water 55:45	Distill continuously at an R/Rmin ratio of 1.25. Ethyl alcohol and water were selected as light and heavy key components
P-23 / C-102	Distillation continuous column	Do the recovery of the ethanol/water 55:45 that is still in the stream from the previous distillation column P-21 / C-101	Distill continuously at an R/Rmin ratio of 1.25. Ethyl alcohol and water were selected as light and heavy key components
P-22 / DDR-101	Drum drying	Dry the stream that	Final solids

		contains mostly cellulose and low amounts of lignin and hemicellulose. Cellulose is considered as product	temperature: 30°C and dry at a rate of 40 kg/m ² h
P-24 / R-104	Continuous Kinetic Reaction	Due to the removal of ethanol lignin is precipitated as the solubility of lignin decreases	Out stream of the reaction: hemicellulose (50% xylose) lignin (80% is dissolved), cellulose(5% dissolved)
P-29 / HX-101	Heat Exchanger	Cool down gas stream from P-16 / V-105 to recirculate to the organosolv process in P-13 / R-103	Cool with cooling water to 50 °C
P-27 / FSP-101	Splitter	Divide stream to recover EtOH/water in the washing step and in the organosolv process	Split flow of streams. Split 19% to top stream.
P-25 / DDR-102	Drum drying	Dry the stream that contains mostly lignin and low amounts of cellulose and hemicellulose. Solid lignin is considered as product	Final solids temperature: 30°C and dry at a rate of 40 kg/m ² h
P-28 / MX-108	Mixer	Mix streams from both distillation columns and flash process containing EtOH/water 55:45	-

1. EQUIPMENT SUMMARY (2015 prices)

Name	Type	Units	Standby/ Staggered	Size (Capacity)		Material of Construction	Purchase Cost (€/Unit)
R-101	Stirred Reactor	1	0/0	21,957.35	L	SS316	620,000
BC-101	Belt Conveyor	1	0/0	100.00	m	CS	204,000
SC-101	Screw Conveyor	1	0/0	15.00	m	CS	24,000
MX-102	Mixer	1	0/0	9,708.79	kg/h	CS	0
V-101	Flash Drum	1	0/0	191.15	L	CS	2,000
RVF-101	Rotary Vacuum Filter	1	0/0	0.99	m2	CS	27,000
V-102	Blending Tank	1	0/0	1,682.79	L	SS316	157,000
MX-103	Mixer	1	0/0	10,200.97	kg/h	CS	0
R-102	Stirred Reactor	1	0/0	3,876.70	L	SS316	486,000
V-104	Decanter Tank	3	0/0	46,231.30	L	SS316	247,000
R-103	Stirred Reactor	1	0/0	25,260.92	L	SS316	642,000
RVF-102	Rotary Vacuum Filter	1	0/0	0.86	m2	CS	27,000
V-106	Blending Tank	1	0/0	1,829.76	L	SS316	159,000
V-105	Flash Drum	1	0/0	312.56	L	CS	3,000
DDR-101	Drum Dryer	2	0/0	11.23	m2	SS316	101,000
MX-104	Mixer	1	0/0	10,954.70	kg/h	CS	0
C-101	Distillation Column	1	0/0	3,022.97	L	CS	15,000
C-102	Distillation Column	1	0/0	2,158.03	L	CS	22,000
R-104	Stirred Reactor	1	0/0	2,151.74	L	SS316	448,000
DDR-102	Drum Dryer	2	0/0	11.48	m2	SS316	102,000
RVF-103	Rotary Vacuum Filter	1	0/0	18.85	m2	CS	87,000
RVF-104	Rotary Vacuum Filter	1	0/0	13.62	m2	CS	76,000
MX-101	Mixer	1	0/0	8,567.19	kg/h	CS	0
MX-105	Mixer	1	0/0	8,554.60	kg/h	CS	0
FSP-101	Flow Splitter	1	0/0	8,216.66	kg/h	CS	0
MX-106	Mixer	1	0/0	1,688.51	kg/h	CS	0
MX-107	Mixer	1	0/0	11,457.38	kg/h	CS	0
MX-108	Mixer	1	0/0	10,414.19	kg/h	CS	0
GR-101	Grinder	1	0/0	1,141.60	kg/h	CS	59,000
HX-102	Condenser	1	0/0	22.31	m2	CS	26,000