

Bachelor Research Project Chemical Engineering Degree
Large Scale Lignin Organosolv Extraction



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16th June 2020

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Word Count: 4878

DISCLAIMER

This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

ACKNOWLEDGEMENTS

I would like to acknowledge the help provided by PhD. Douwe Zijlstra during this research project.

ABSTRACT

Three chemical plant designs were investigated to extract lignin from 10 tonnes of walnut shells annually by organosolv extraction. Two of those plants are identical in structure, however the difference lays in the extraction method used. One plant has a batch extraction system whereas the other plant utilises a flow through extraction. The extraction is done in batches of 5.7 tonnes and a mixture of ethanol and water (80:20) as solvent. The conditions used for the extraction are 80°C at 6 bar for 5 hours, which yielded annually 2000 tonnes and 2370 tonnes of organosolv lignin respectively. Furthermore, in the third plant, the extraction method used was a flow through, however the process was done in 3 hours at 120°C and 6 bar. This process also yielded 2370 tonnes of organosolv lignin.

A piping and instrumentation diagram (P&ID), was made for the whole process to have a general overview of the instrument used to control each equipment used in the plant. Furthermore, a Hazard and Operability (HAZOP) study was conducted to further identify any potential risks. The study was then used to install additional safeguards to lower these risks in the plant.

Multiple issues arose when modelling in Aspen plus, mainly that lignin is not a compound present within the Aspen database. Therefore, many assumption had to be made, as a result of such, any values obtained for the duty and stream composition are regarded as inaccurate. Despite that, the simulation does provide a relative estimate of the extraction processes.

A financial analysis was done to compare which plant is more economically viable. From this analysis, it was found that at the same operating conditions, a batch extraction is more economically favourable. However, if one were to operate the plant at elevated temperature, 120°C, for a shorter period of time, the flow through process is more economically interesting.

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I. INTRODUCTION

Juglans regia L., more commonly known as walnut, is a nut from any tree of the genus *Juglans*. [1] These nuts originated in the Mediterranean region and central Asia and have been part of the human diet for millennia. These nuts are rich in omega-3 fats and contain higher amounts of antioxidants than most other food.[2] In 2018 to 2019, in the United States of America only, about 613 metric tonnes of these nuts are produced. Approximately 50% by mass of the produced walnuts are discarded as these are uneatable shells. However, it was found that these shells can be used as a natural biomass for the production of lignin. Especially since according to [3], these shells are composed of 49.1% of lignin.

Lignin is an aromatic complex polymer of monolignols rich in aromatic rings which is found in plant cell walls. However, it is currently impossible to define a precise structure of lignin as the aromatic units are randomly linked throughout the polymer. It is not composed of carbohydrate monomers whereas the rest of polymers found in plant cell walls are composed of carbohydrate monomers. [4] This natural polymer is currently exclusively used for producing energy, however depending on the purity of the final product, it could potentially in other high value products such as carbon fibres.

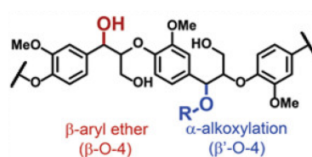


Figure 1. Structure of Lignin [7]

Organosolv extraction is the process of cooking the lignocellulosic biomass in a mixture of water with an organic solvent and an acid catalyst which results into the deconstruction of both lignin and hemicellulose and its dissolution in the cooking liquor. Furthermore, It has been shown that using acids during the organosolv process allows for an effective dissolution of hemicelluloses contained in the biomass, liberating lignin.[15] More importantly, the extraction is performed at elevated pressure to maintain the organosolv solvent completed liquid at higher temperature especially since lignin is hydrophobic. The obtained lignin is then typically retrieved as a precipitate by dilution of the liquor with water. This extraction process will produce three distinct stream; a lignin rich solid precipitate, a cellulose-much pulp and a hemicellulose rich liquid. Normally, the organic solvent can be recycled by distillation from the liquid stream. [5]

The aim of this research project, is to design and compare on an economical perspective three different organosolv extraction plants. One plant will be equipped with a batch reactor extraction vessel whereas, another will have a flow through extraction system. In order to be able to fairly compare these two plants, they will have identical inlets, 10000 tonnes per annum of walnut shells, and identical solvent conditions, 80:20 mixture of ethanol to water at 80°C at 6 bar for 5 hours. In the third plant, a flow through system with identical solvent will be designed, however the process will operate at elevated temperature, 120°C, but shorter extraction time, 3 hours. The extraction values for the upscaling will be based off the laboratory data provided by the University of Groningen, more accurately Peter Deuss research's group, more accurately by Douwe Zijlstra.

II. PROCESS DESCRIPTION

II.1 BLOCK DIAGRAM

The specification for the designed chemical plant which extracts lignin from walnut shells are as follows. The capacity of the plant is 10000 tonnes per annum (10 kTpA). This was subsequently divided into 1752 batches of 5.7 tonnes per year. This translates to approximately 5 batches per day with 5 hours batches.

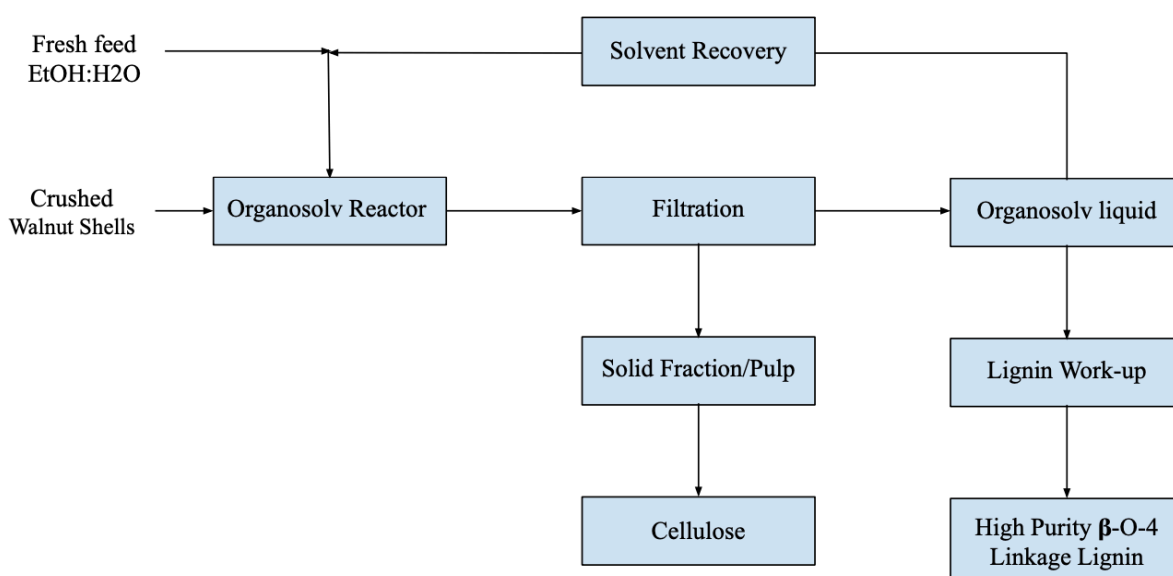


Figure 2. Block diagram for the Organosolv Extraction of lignin

The process for the extraction of lignin from woody biomass followed the following block diagram proposed. The initial inlet of raw woody biomass, in this case walnut shells, must be initially pretreated prior to the Organosolv extraction. This pretreatment is subdivided into particles size preparation and extractive removal. The raw walnut shells enter an industrial milling machine in order to be milled to particle sizes of 2 mm. Once the inlet biomass was crushed and milled to the desired size, the extractives such as fats, waxes, proteins were removed. The extractives in biomass are often referred to the non-structural components which can be extracted by solvents such as ethanol and toluene[6]. After having pretreated the biomass, the loading of the reactor can occur. The organosolv solvent used in the extraction of the lignin from walnut shells is an acidic mixture of 80:20 ethanol to water. After the desired extraction time has elapsed, the solid fraction, mainly containing cellulose, is filtered off and the obtained liquid fraction is evaporated in order to recover the solvent used. The lignin obtained after the evaporation is worked up through precipitation and high purity β -O-4 linkage lignin is obtained.

II.II PROCESS FLOW DIAGRAM

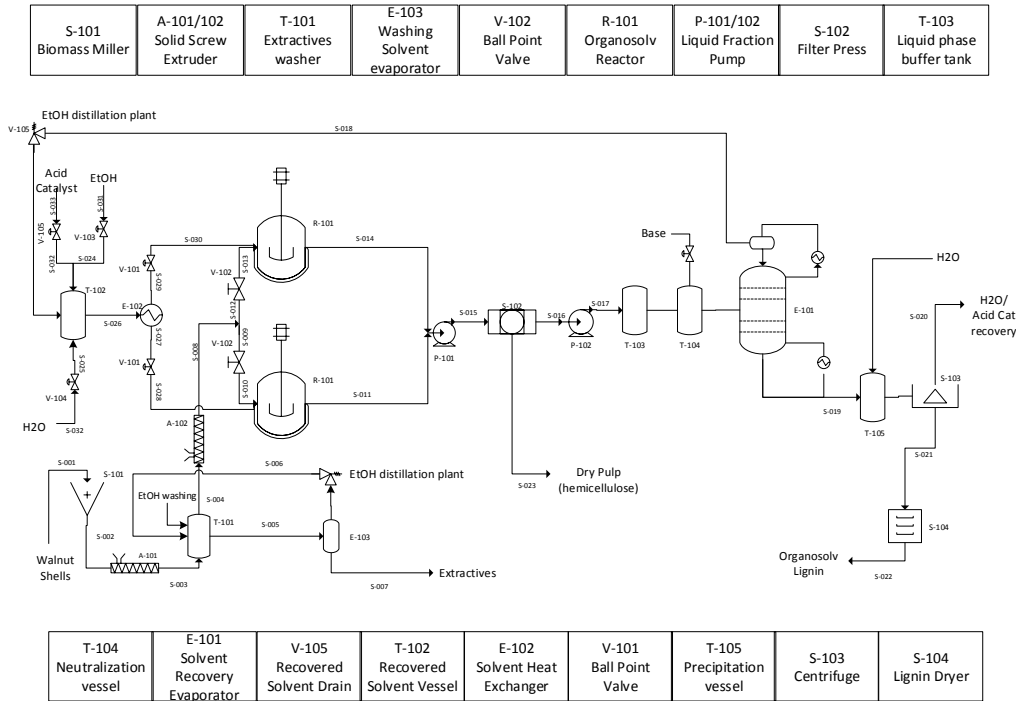


Figure 3. Process Flow Diagram for the plant

The previous block diagram has been translated into the process flow diagram (PFD) presented above. As mentioned previously in the block diagram, the biomass inlet, the walnut shells, of 5.7 tonnes have to be pretreated. The pretreatment occurs when the walnut shells are milled in an industrial impact mill S-101 into fine particles of approximately 2 mm [7]. Once the walnut shells are finely ground, the shells are extruded into vessel T-101 where the extractives will be removed. The removal of the extractives is done by washing the biomass in a pressure vessel T-101 with ethanol at 80°C and 20 bar for 20 minutes. [8] The ethanol was then removed by filtration and the walnut shells were subsequently dried in an oven. The washing solvent can be recovered by evaporation in E-103 and cooled back to the temperature in the pressured vessel T-101. After 100 pretreatment washes, the solvent is drained out of the system and sent to an external distillation plant for purification.

Once the pretreated walnut shells are dried, the 5.7 tonnes of pretreated shells are loaded into an organosolv reactor vessels R-101, either a batch reactor (BR) or a plug flow reactor (PFR), for lignin extraction. The solvent used for this organosolv extraction is mixture of ethanol with water in a ratio of 80:20 accompanied by 0.18 M sulphuric acid catalyst. The extraction conditions set within the reactor vessel are 80°C and 6 bar for 5 hours or 120°C at 6 bar for 3 hours (PFR-2). The solvent is prepared in T-102 and is brought to the extraction condition by E-102. The purpose of the elevated pressure is to ensure that the ethanol in the solvent remains liquid throughout the extraction as lignin is only soluble in ethanol. The usage of two extractors in parallel was done in order to decrease the down time of the plant. This is because as one extractor is being emptied and prepared for the next extraction, meanwhile the other extractor can run.

After the extraction has been completed, the content of the reactor is pumped by P-101 out into a filter press S-102, where the liquid phase is separated from the solid phase, containing mainly of holocellulose. The liquid phase was then neutralised in vessel T-104 prior to being sent to a distillation column E-101 in order to recover the maximum amount of solvent whilst keeping the lignin soluble. Once the maximum amount of solvent is recovered, the remaining soluble lignin is precipitated by the addition of water in vessel T-105. Finally, the pure lignin is obtained by filtration of water and acid through centrifugation S-103 followed by the air drying of the lignin in an air oven S-104 at 85°C over night.

II.III PIPING AND INSTRUMENTATION DIAGRAM

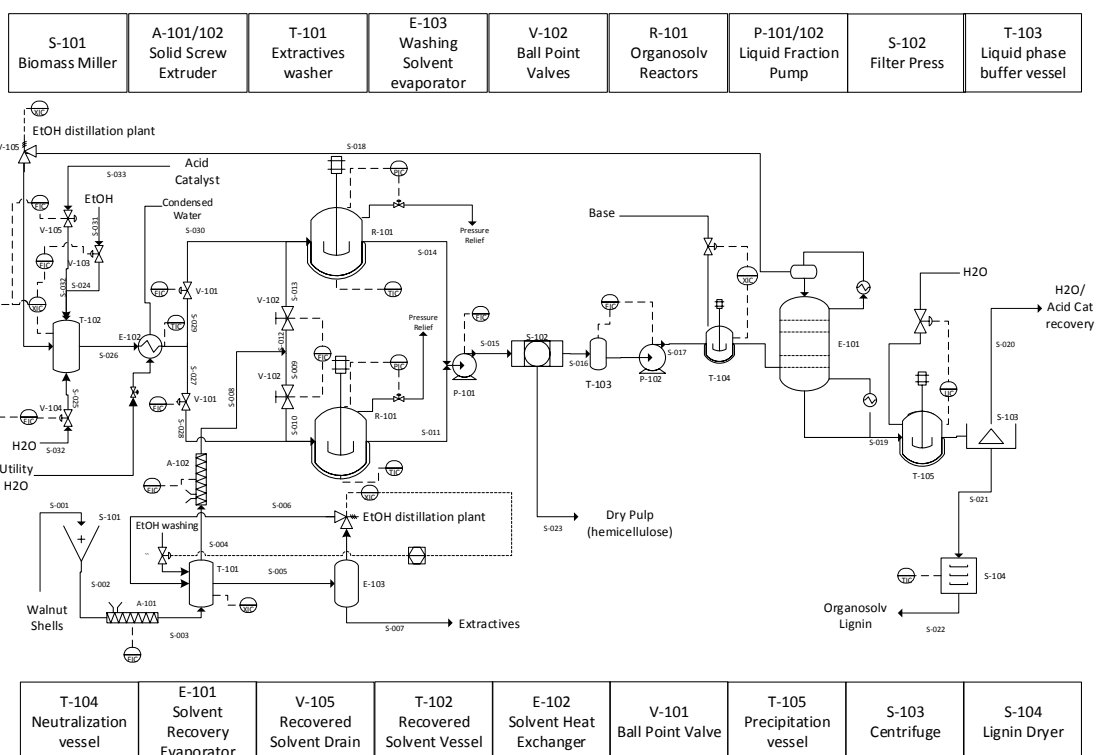


Figure 4. Piping and Instrumentation Diagram (P&ID) for the process

In this subsection, the instrumentation used in the P&ID above will be explained. The solid biomass is transported by extruders A-101 and A-102. These equipments are electronically connected to flow indicator and controller (FIC). This is done in order to maintain a constant inlet of shells throughout the process. In the pretreatment, the pressured vessel T-101 conducts the washing of the extractives at 80°C and 20 bar. These conditions have to be monitored and controlled by a temperature and a pressure indicator and controller (TIC and PIC, respectively). In order to recover the solvent from the washing liquor, a distillation column is used. Similarly to the pressured vessel, a TIC is installed in order to ensure that the required temperature is attained. Once the solvent is recovered by evaporation, the purity of the solvent is controlled by an XIC, where X stands for composition. If the recovered solvent is found to be too contaminated, the XIC electronically controls a drain which flushes the solvent out of the system and towards an ethanol purification plant. Simultaneously, an

electrical signal is sent to valve V-106 which opens to feed new fresh washing solvent to the pretreatment system.

For the extraction vessels, the flow of ground pretreated walnut shells to the reactors is controlled by two valves. These valves are connected to a FIC which electronically controls the biomass entering the reactor by opening and closing them accordingly. This type of valve system is also used for the solvent entering the organosolv reactor as seen in stream S-029 and S-027. The organosolv extractor vessels operate at 80°C and 6 bar. These conditions are monitored and controlled by a TIC and PIC. The TIC is connected to a heating jacket which maintains the temperature of the extraction vessel. The liquid phase is pumped by the use of pumps P-101 and P-102. These pumps are connected to a FIC in order to maintain a constant flow throughout the system. Prior to entering the evaporator, the liquid phase is neutralised in T-104. This vessel is connected to a XIC, where X is pH, which regulates the flow of base. In the solvent recovery column, E-101, a combination of different controllers are used as seen in appendix A, however the main ones are a PIC and TIC. These are connected to the evaporator to ensure that the desired temperature and pressure is maintained. This is because any small deviation will either result with increased costs due to excess solvent waste or lost of insoluble lignin in the recovery column. The recovered ethanol passes through a valve V-105 where an XIC, where X is composition, is connected. If the composition of the recovered ethanol is found to be impure, the valve opens and the solvent is drained out of the system and sent to an external distillation plant for purification. Therefore, in order to maintain the ratio of solvent consistent throughout the process, in vessel T-102, a composition indicator and controller is installed. This controller controls the FIC on the valves attached on each solvent component feed, opening them to attain the desired composition of solvent. In T-105, a level indicator and controller, represented as LIC in the figure 4, is installed. To successfully perform the precipitation reaction, this controller manipulates the flow of water into the vessel. Finally, the obtained organosolv lignin is dried in an oven S-104 connected to a TIC to ensure that the correct temperature is maintained.

II.IV HAZARD AND OPERABILITY ANALYSIS

Node	Deviation	Cause	Consequence	Before Risk Reduction			Effective Safeguards	Responsibility	After Risk Reduction		
				S	L	RR			S	L	RR
1. E-102	Limited cooling water flow	Pipe blockage Cooling water valve malfunction	Increase in temperature of exiting solvent, resulting in undesired product from the reaction in R-101a/b.	3	3	9	Implement a new bypass in the cooling water stream. Implementation of two flow indicator and controller in the bypass and original cooling water stream Link a temperature controller in the outlet solvent flow which may open the bypass in case of rapid temperature increase	Safety Operator	2	3	6
	Corrosion of the cooling water pipeline	Hardness of the cooling water	Decrease in cooling of the solvent Possible rupture of the cooling water pipeline	3	2	6	More regular and proper maintenance	Operators	3	1	3
	Process fluid contamination	Leakages within the heat exchanger and cooling water goes into the process fluid	Altering the solvent ratio and thus decreasing the efficiency of the process	4	2	8	Proper maintenance and implementation of an operator alert in the block	Operator	4	1	4

Table 1. HAZOP analysis Table

A Hazard and Operability study (HAZOP) was performed on one equipment in the process. The chosen equipment was heat exchanger E-102 used to bring the solvent to the operating conditions of the organosolv extraction. The first deviation chosen was limited cooling water flow. This could be caused by a

pipe blockage in the cooling water system or even by a cooling water valve malfunction. Due to the decreased amount of cooling water supplied, the temperature of the solvent will increase, resulting in the undesired extraction condition of lignin. This increased temperature will produce worse quality organosolv lignin which is undesired and less valuable. Therefore, applying the risk reduction matrix, the deviation was found to be equivalent to a 9, so new effective safeguards have to be implemented. The first safeguard implemented is the creation of a bypass in the cooling water stream which is automatically opened when an irregularity in cooling water flow is detected. This then directly links to the second safeguard which is the implementation of two FIC, one on the bypass and one on the original cooling water system. Both FICs are connected to the same computer which then controls the flow of cooling water necessary. Finally, a final safeguard can be implemented in the form of TIC on the outlet solvent stream. This TIC will be linked to the same computer as the previous two FICs. Therefore, if the outlet temperature of the solvent was to diverge from the desired temperature, the FICs will adjust the flow of cooling water accordingly.

Another deviation that could occur in the process is the corrosion of the cooling water pipes due to its hardness. A consequence of this, would be the presence of cracks or even ruptures in the pipeline delivering the water, which in turn will result in a less efficient cooling. The severity of this deviation was given a 3 whereas the likelihood is given a 2 which resulted in a risk rating of 6. Therefore, a possible safeguard to decrease this rating would be to perform more regular and thorough maintenance, thus reducing the likelihood for this to happen.

An additionally deviation that could also occur in E-102 would be the contamination of the process fluid. This could happen if leakages within the heat exchanger are present and cooling water is then mixed into the process fluid. This deviation is given a severity of 4, as the solubility of lignin increases with higher concentration of ethanol in the solvent. Therefore, the presence of increased water will decrease the overall lignin extraction efficiency. Despite that, the likelihood of leakages in the heat exchanger is relatively low at 2. As a result, proper maintenance must be done and the implementation of a composition indicator in the outlet stream can be seen as effective safeguards. The composition indicator is linked to an alert within the operation room.

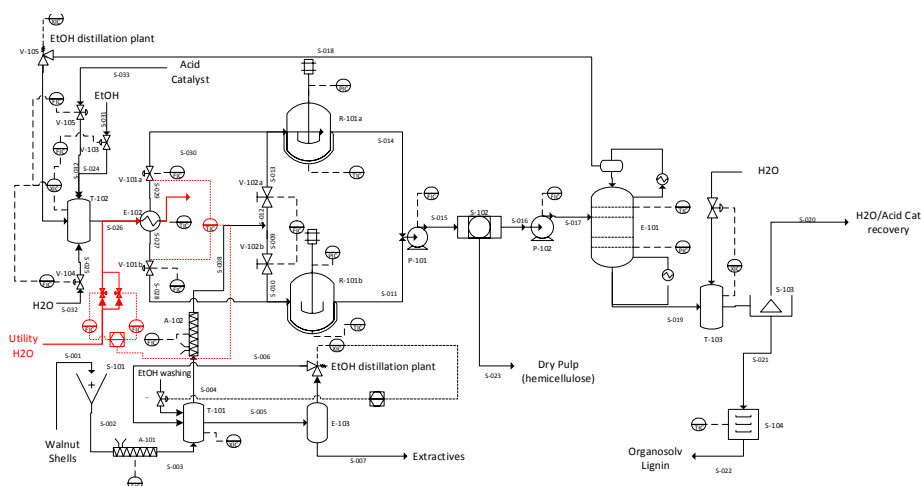


Figure 5. Improved P&ID with HAZOP safeguards (in red)

III. PROCESS MODELLING

Aspen Plus is a software used to model different types of chemical processes [9], thus, it was used to design the organosolv extraction of lignin from ground pretreated walnut shells. One major issue arose when modelling the extraction, lignin was not present in the Aspen database. The Aspen databanks are filled with what are known as “common” substances where lignin cannot be found. Nevertheless, its structure could be imported into Aspen, unfortunately, Aspen’s modelling system is strongly based on the binary interactions. However, those interactions for lignin are currently unknown as no definite structures exists. As a result of such, literature data of the extraction process provided by [7] was used to estimate the production of organosolv lignin on a larger scale. However, the solvent recovery and work up will be modelled in Aspen.

The property package used in the modelling is Peng-Rob. This is because this property package is found to be the most enhanced model in Aspen. Especially since it has the largest applicability in range in terms of temperature and pressure. Furthermore, this specific property package has the largest binary interaction parameter database available on Aspen.[10]

III.I ASPEN MODELLING - Upscaling

As stated above, the values for the extraction have been scaled up from the data provided by the laboratory. Hence, the table below will have the upscaled laboratory data for both the flow through and batch reactor setup. [4][7]

<i>Component</i>	<i>Literature</i>	<i>Upscale</i>
Walnut Shells	20 g	5.7 tonnes
Initial Lignin	9.82 g	2.79897 tonnes
Holocellulose	9.32 g	2.6562 tonnes
Ash	0.72 g	0.2052 tonnes
Extractives	0.14 g	0.0399 tonnes
Organosolv Extraction Data -BR- 80°C, 5hrs		
Ethanol	160 mL	45600 L
Water	40 mL	11400 L
0.18M H ₂ SO ₄	2.5 mL	712.5 L
Organosolv Lignin	4.015 g	1.144 tonnes
Dry Pulp (Cellulose)	7 g	1.995 tonnes

Table 2. Upscale Batch Reactor Data per batch

Organosolv Extraction Data - PFR - 80°C, 5hrs		
Ethanol	271.2 g	77.296 tonnes
Water	67.8 g	19.324 tonnes
0.18M H ₂ SO ₄	5 mL*	1425 L*
Organosolv Lignin	4.746 g	1.35261 tonnes
Dry Pulp (Cellulose)	7 g	1.995 tonnes
Organosolv Extraction Data - PFR II - 120°C, 3 hrs		
Ethanol	271.2 g	46.378 tonnes
Water	67.8 g	11.594 tonnes
0.18M H ₂ SO ₄	5 mL*	855 L
Organosolv Lignin	4.746 g*	1.353 tonnes*
Dry Pulp (Cellulose)	7 g	1.995 tonnes

Table 3. Upscale Flow Through Reactor Data per batch (*estimated values)

Secondly, using the extraction values obtained from upscaling the laboratory data, the amount of recovered solvent has to be determined. Initially, the solubility of lignin in a mixture of 80:20 ethanol to water has to be found. This is because the extracted organosolv lignin has to remain soluble after the recovery column. According to the experiment performed in the laboratory, at the desired extraction conditions, the solubility of lignin was found to be around 80 g/L. Thus, from this solubility value, the quantity of recovered solvent was calculated, as shown in table 4.

Batch Reactor Setup - 80°C, 5 hrs		
	Volume of solvent (L)	Flow rate of Solvent (L/min)
Used in Extraction	57000.0	1900
Required for soluble	14303.1	476.77
To be recovered	42696.9	1423.23
Flow Through Setup - 80°C, 5 hrs		
	Volume of solvent (L)	Flow rate of Solvent (L/min)
Used in Extraction	120317.6	401.059
Required for soluble	16907.4	56.358

To be recovered	103410.1	344.701
Flow Through Setup - 120°C, 3 hrs		
	Volume of solvent (L)	Flow rate of Solvent (L/min)
Used in Extraction	72190.6	401.059
Required for soluble	10144.4	56.358
To be recovered	62046.2	344.701

Table 5. Solvent Recovered

It is important to mention that for the batch reactor extraction process, the content is estimated to be emptied within 30 minutes, resulting in a liquid flow of 1900 l/min. Furthermore, having determined that solvent can be recovered in these processes, an Aspen simulation was created as seen in the figure below. Additionally, due to the similarity in the processes, the same flowsheet design was used in the solvent recovery and work-up simulations.

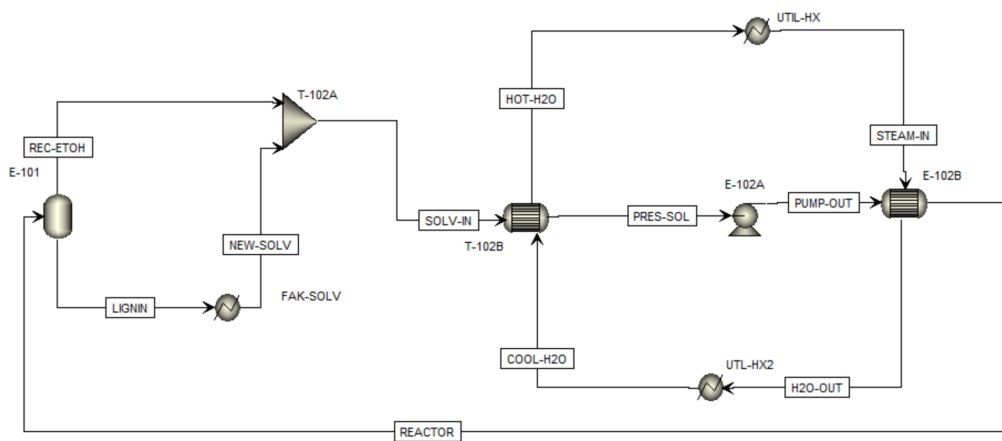


Figure 6. Aspen Simulation Flowsheet

III.I.I ASPEN MODELLING - Simulation

As mentioned previously, the same Aspen flowsheet was used for the three different simulations. In the first block, E-101, a sensitivity analysis was performed in order to determine the temperature at which the excess ethanol is evaporated at 2 bar of pressure. Secondly, to confirm the results of the sensitivity analysis done by Aspen, the molar flow of ethanol being recovered was manually calculated. From those specifications, the evaporator was designed accordingly.

After having recovered the solvent through evaporation, the new solvent had to be worked back up to the extraction conditions. In order to simulate the addition of fresh new solvent, a heater named FAK-SOLV was used to bring the collected solvent with lignin back to atmospheric conditions. The newly formed solvent mixture had to be cooled, by use of a heat exchanger T-102B, prior to compression due to the partial

vaporisation of the solvent. Once the solvent was fully liquefied, pump E-102A was used to increase the pressure of the system to 6 bar. Finally, after pressurisation, the solvent has to be heated by E-102B up to the desired temperature for the extraction.

The data for the relevant duty obtained from Aspen have been simplified in the table below.

<i>Batch Reactor - 80°C, 5 hrs</i>	
<i>Equipment</i>	<i>Duty (kW)</i>
<i>E-101</i>	<i>19779.100</i>
<i>T-102B</i>	<i>20256.652</i>
<i>E-102A</i>	<i>21.500</i>
<i>E-102B</i>	<i>1939.397</i>
<i>PFR - 80°C, 5 hrs</i>	
<i>Equipment</i>	<i>Duty (kW)</i>
<i>E-101</i>	<i>5585.611</i>
<i>T-102B</i>	<i>5620.610</i>
<i>E-102A</i>	<i>6.760</i>
<i>E-102B</i>	<i>212.962</i>
<i>PFR - 120°C, 3 hrs</i>	
<i>Equipment</i>	<i>Duty (kW)</i>
<i>E-101</i>	<i>4704.438</i>
<i>T-102B</i>	<i>5620.610</i>
<i>E-102A</i>	<i>6.760</i>
<i>E-102B</i>	<i>1094.077</i>

Table 6. Relevant duty for the Equipment from Aspen

From the simulation performed by Aspen Plus, the following solvent recovery and energy rating have been calculated. It is possible to see that the flow through processes have increased solvent recovery compared to the batch extraction. This is mainly due to the increased extraction yield as mentioned in table 4. However, the batch reactor extraction has a lower energy rating compared to the flow through extractions. This could be predicted as less solvent is evaporated in the batch process compared to the flow through.

Extraction method	Batch Reactor	Flow Through - 80°C, 5 hrs	Flow Through - 120°C, 3 hrs
Solvent Recovered (%)	74.9	86.0	86.0
Energy Rating (MW/hr)	9.9	27.95	13.11

Table 8. Results for solvent recovery in Aspen

Refer to appendix B for the breakdown of each heat exchanger area obtained from Aspen.

IV. FINANCIAL ANALYSIS

The financial analysis is the final but yet the most crucial step in designing a plant, as after all, chemical plants are built to make a profit. Cost estimation is a key segment in determining the profitability of the project. [12] Therefore, to estimate the total capital costs, the fixed capital investment and the working capital have to be calculated. Fixed capital investment is subdivided into the following: Inside Battery Limits (ISBL) investment - the cost of the plant itself, modifications and improvements to the site infrastructure (offsite (OSBL) investment), engineering and construction costs and contingency charges. The ISBL Plant Costs entail all the major process equipment, bulk items, installation labor and supervision [12]. The Offsite Costs (OSBL) include the costs of additions that must be made to the infrastructure. [12] Design and Engineering costs are composed of costs for detailed design and other engineering services required to complete the project. Finally, the final cost which comprises the fixed capital costs is the contingency charges which are extra costs added into the budget to allow for variation from the costs estimate. These variation could be caused by changes in prices, currency fluctuations, minor changes in the project scope and other unexpected problems [12].

The costs for the major process equipment have been calculated by the proposed Cost Curve estimation, eq 7.9 Sinnott and Towler [12]. However, the use of this equation relied strongly on data obtained from Aspen such as the heat exchanger area and due to the previously mentioned drawbacks of Aspen, some estimation may not be very accurate.

$$C = A + B \times S^n, \text{ Eq 7.9 [12]}$$

The installation cost vary depending on the process type. As the majority of the process can be seen as a Mixed Fluids-Solid Processing plant, a Lang Factor of 3.63 was taken for the final ISBL calculation. This resulted in a total value of around 13.5 million USD for the batch process and 17.3 million USD for the flow through processes, as can seen from the table below. Furthermore, due to the relative novelty of the process, the OSBL, Design and Engineering and Contingency costs were estimated to be at 40, 20 and 25 percent of the ISBL respectively. This resulted in the overall Fixed Capital Investment of 24.9 million USD for the Batch Process and 32.1 million USD for the flow through setups, as can be seen in the table below.

	Batch Process	Flow Through Process - I	Flow Through Process - II
ISBL	\$13,454,457.06	\$17,329,576.44	\$17,329,576.44
OSBL	\$5,381,782.82	\$6,931,830.58	\$6,931,830.58
D&E	\$2,690,891.41	\$3,465,915.29	\$3,465,915.29
Contingency	\$3,363,614.27	\$4,332,394.11	\$4,332,394.11
Fixed Capital Inv.	\$24,890,745.56	\$32,059,716.41	\$32,059,716.41

Table 7. Breakdown of Fixed Capital Investment for Batch Process and Flow Through Process

Furthermore, in order to try and estimate the time for return on investment, the material cost, utility cost and energy cost have been estimated on the current market price. Additionally, the equipments are predicted to have a shelf life of approximately 10 years before requiring replacement. The tables below will illustrate the total cost of operating an organosolv plant. More importantly, the cost for employment and taxes are not included in the calculation for determining the yearly costs as these are currently unknown.

Cost	Batch Process	Flow Through Process - I	Flow Through Process - II
Total chemical cost	\$16,629,538.52	\$20,049,335.03	\$12,034,793.95
Capital cost	\$370,646.20	\$477,398.80	\$477,398.80
Duty cost	\$627,163.44	\$1,076,023.81	\$1,076,023.81
Yearly Costs	\$17,627,348.16	\$21,602,757.64	\$13,588,216.55

Table 8. Annual operational for Organosolv Plant

Based on the annual costs, if one were to aim for a return on investment within 7 years, the organosolv lignin produced in the batch process plant needs to be sold at 8.8 thousand USD per tonnes whereas for the flow through process at the same conditions, the organosolv lignin has to be sold for 9.1 thousand USD per tonnes in order to break even. However, for the organosolv lignin produced by the flow through process at elevated temperature, system II, the sale price is the lowest at 5.7 thousand USD. Unfortunately, according to [13], the current organosolv lignin market is valued at 850 dollar per metric tonnes. Therefore, if the organosolv lignin were to be sold according to the actual market value, the annual income per plant can be seen in the table below.

Income	Batch Process	Flow Through - I	Flow Through - II
Organosolv Lignin	\$1,042,480.30	\$1,232,281.81	\$1,232,281.81
Cellulose	\$3,058,335.00	\$3,058,335.00	\$3,058,335.00
Total income	\$4,100,815.30	\$4,290,616.81	\$4,290,616.81

Table 9. Annual income on products from plant

Due to the excessively high solvent cost and low market price of the products made, the plant will be in deficit no matter the process type. In the BR process, the plant is expected to make an annual deficit of 12.9 million USD, whereas in the flow through processes, the plant is expected to make a yearly deficit of 16.5 million USD and 8.5 million USD respectively. Furthermore as stated by [14], no current large scale organosolv plants are existent as most of them have filled for bankruptcy.

V. CONCLUSION

Due to the relative novelty of this process, one main disadvantage was the lack of data in the Aspen database. This has heavily hindered the accuracy of the plant design as several assumptions had to be made. In order to be able to accurately model the organosolv extraction of lignin, more kinetic data are required in particular. These kinetic data will allow Aspen to be able to extrapolate the binary interactions required to simulate this process. As a result of these improvements, the overall accuracy of the process will improve. This is especially important for the financial analysis as improving the reliability of the model may be difference between bankruptcy and profitability.

The extraction of lignin from pretreated ground walnut shells by Organosolv was modelled according to the following estimations. The first estimation was that the up scaling factor was maintained through the whole extraction process. The ratio of solvent to mass of biomass is maintained the same during the upscaling in order to obtain the same efficiency. The extraction conditions used are 80°C at 6 bar of a 80:20 ethanol water mixture which in turns resulted in a 20% organosolv lignin mass extracted in the batch process and 24% organosolv lignin mass in the flow through processes. As the process was modelled for an initial inlet of 10 kTpa of walnut shells, this resulted in 2000 tonnes per annum of organosolv lignin for the batch process and 2370 tonnes per annum for the flow through processes.

For the performed financial analysis, due to the estimations throughout the modelling, the estimated costs may differ greatly from the actual costs. The equipments in the process are expect to have a lifespan of 10 years before required to be replaced. With the current market and production of organosolv lignin, the plant with a batch extraction will make a deficit of 12.9 million USD. Whereas, for the flow through organosolv extraction, this type of organosolv plant will make a deficit of 16.5 million USD annually. However, if one were to improve the economical viability of this plant, a solution would be to operate at higher temperature for a shorter period of time. As shown in the financial analysis, the annual cost for operating such a plant will be around 8.5 million USD.

As this is relatively new study, further improvements should be done. As limited data is currently available for these types of extractions, more research should be done in doing a dual extraction system. This system entails an initial flow through extraction by Organosolv, at elevated conditions followed by a harsher extraction to obtain the highest yield of sellable product. Additionally, research could be done into utilising a different alcoholic solvent for the extraction. Especially as the current price of the product being produced is equal to that of the solvent being used. An interesting alternative would be to use methanol as solvent instead of ethanol due to its relatively cheap price and similar extraction efficiency. However, by doing so, it is important to remember that using methanol is less environmentally friendly and newer plant safety have to be redesigned. Finally, another future prospect for this plant design would be to use the distillation column within the plant to recover the solvent used in the process, instead of using an external contractor. This will greatly decrease the solvent cost of the plant and hopefully make this process more economically interesting.

VI. WORK CITED

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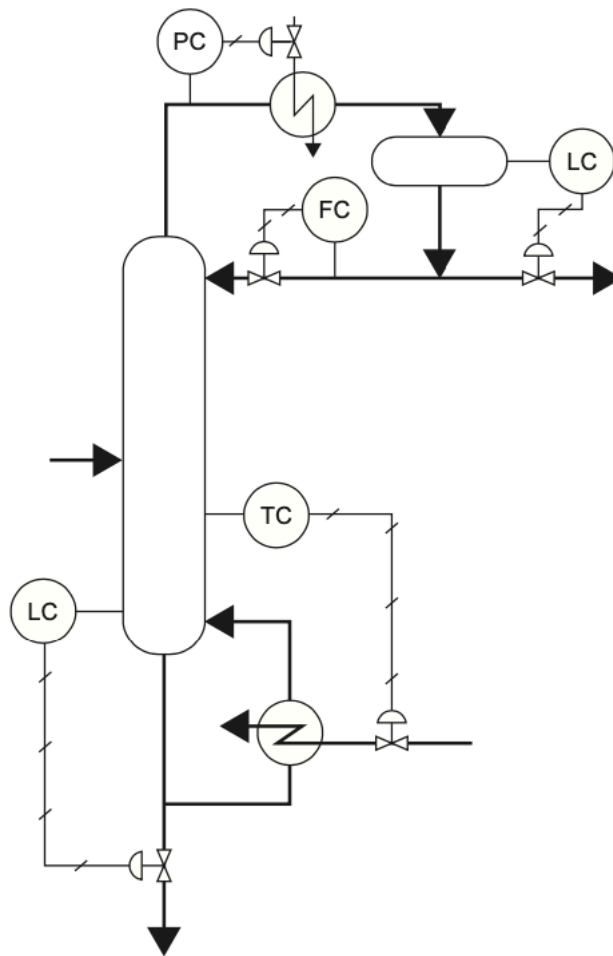
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VII. APPENDIX

APPENDIX A - P&ID PARTIAL DISTILLATION COLUMN

P & ID for partial distillation column originating from [16]



APPENDIX B - HEAT EXCHANGER DETAILS

The area for the heat exchangers used in the simulation have been simplified in the table below.

<i>BR - 80°C, 5 hrs</i>	
<i>Equipment</i>	<i>Area (m²)</i>
<i>T-102B</i>	<i>1576.7</i>
<i>E-102B</i>	<i>129.753</i>
<i>PFR - 80°C, 5 hrs</i>	
<i>Equipment</i>	<i>Area (m²)</i>
<i>T-102B</i>	<i>197.994</i>
<i>E-102B</i>	<i>17.753</i>
<i>PFR - 120°C, 3 hrs</i>	
<i>Equipment</i>	<i>Area (m²)</i>
<i>T-102B</i>	<i>197.994</i>
<i>E-102B</i>	<i>52.7262</i>

Table 7. Heat exchanger area from the simulation in Aspen

Appendix B.1 Aspen data for BR-80

Main Flowsheet × T-102B (HeatX) - Thermal Results × E-102B (HeatX) - Thermal Results × +					
Summary Balance Exchanger Details Pres Drop/Velocities Zones Utility Usage Status					
Heatx results					
Calculation Model: Shortcut					
Inlet			Outlet		
Hot stream:	SOLV-IN		PRES-SOL		
Temperature:	72,4493	C	57,2343	C	
Pressure:	1	bar	1	bar	
Vapor fraction:	0,716382		0		
1st liquid / Total liquid	1		1		
Cold stream:	COOL-H2O		HOT-H2O		
Temperature:	25	C	70	C	
Pressure:	1	bar	1	bar	
Vapor fraction:	0		0		

Exchanger details		
▶ Calculated heat duty:	2,02567e+07	Watt
▶ Required exchanger area:	1576,79	sqm
▶ Actual exchanger area:	1576,79	sqm
▶ Percent over (under) design:	0	
▶ Average U (Dirty):	850	Watt/sqm-K
▶ Average U (Clean):		
▶ UA:	1,34027e+06	J/sec-K
▶ LMTD (Corrected):	15,1138	C

Exchanger details for T-102B

Main Flowsheet × T-102B (HeatX) - Thermal Results × E-102B (HeatX) - Thermal Results × +					
Summary Balance Exchanger Details Pres Drop/Velocities Zones Utility Usage Status					
Heatx results					
Calculation Model: Shortcut					
Inlet			Outlet		
Hot stream:	STEAM-IN		H2O-OUT		
Temperature:	90	C	85,7189	C	
Pressure:	1	bar	1	bar	
Vapor fraction:	0		0		
1st liquid / Total liquid	1		1		
Cold stream:	PUMP-OUT		REACTOR		
Temperature:	57,3706	C	80	C	
Pressure:	6	bar	6	bar	
Vapor fraction:	0		0		

Exchanger details		
▶ Calculated heat duty:	1,94638e+06	Watt
▶ Required exchanger area:	130,039	sqm
▶ Actual exchanger area:	130,039	sqm
▶ Percent over (under) design:	0	
▶ Average U (Dirty):	850	Watt/sqm-K
▶ Average U (Clean):		
▶ UA:	110533	J/sec-K
▶ LMTD (Corrected):	17,609	C

Exchanger details for E-102B

Appendix B.2 Aspen data for PFR-80

Heatx results			
Calculation Model	Shortcut		
	Inlet		Outlet
Hot stream:	SOLV-IN		PRES-SOL
Temperature:	72,4533	C	69,6831 C
Pressure:	1	bar	1 bar
Vapor fraction:	0,867079		0
1st liquid / Total liquid	1		1
Cold stream:	COOL-H2O		HOT-H2O
Temperature:	25	C	50 C
Pressure:	1	bar	1 bar
Vapor fraction:	0		0
1st liquid / Total liquid	1		1

Exchanger details		
Calculated heat duty:	5,62061e+06	Watt
Required exchanger area:	197,994	sqm
Actual exchanger area:	197,994	sqm
Percent over (under) design:	0	
Average U (Dirty):	850	Watt/sqm-K
Average U (Clean):		
UA:	168295	J/sec-K
LMTD (Corrected):	33,3973	C

Exchanger details for T-102B

Heatx results			
Calculation Model	Shortcut		
	Inlet		Outlet
Hot stream:	STEAM-IN		H2O-OUT
Temperature:	90	C	81,3956 C
Pressure:	1	bar	1 bar
Vapor fraction:	0		0
1st liquid / Total liquid	1		1
Cold stream:	PUMP-OUT		REACTOR
Temperature:	51,773	C	80 C
Pressure:	6	bar	6 bar
Vapor fraction:	0		0
1st liquid / Total liquid	1		1

Exchanger details		
Calculated heat duty:	212597	Watt
Required exchanger area:	17,753	sqm
Actual exchanger area:	17,753	sqm
Percent over (under) design:	0	
Average U (Dirty):	850	Watt/sqm-K
Average U (Clean):		
UA:	15090	J/sec-K
LMTD (Corrected):	14,0886	C

Exchanger details for E-102B

Appendix B.3 Aspen data for PFR-120

Heatx results				
Calculation Model: Shortcut				
	Inlet		Outlet	
Hot stream:	SOLV-IN		PRES-SOL	
Temperature:	72,4533	C	69,6831	C
Pressure:	1	bar	1	bar
Vapor fraction:	0,867079		0	
1st liquid / Total liquid	1		1	
Cold stream:	COOL-H2O		HOT-H2O	
Temperature:	25	C	50	C
Pressure:	1	bar	1	bar
Vapor fraction:	0		0	
1st liquid / Total liquid	1		1	

Exchanger details		
Calculated heat duty:	5,62061e+06	Watt
Required exchanger area:	197,994	sqm
Actual exchanger area:	197,994	sqm
Percent over (under) design:	0	
Average U (Dirty):	850	Watt/sqm-K
Average U (Clean):		
UA:	168295	J/sec-K
LMTD (Corrected):	33,3973	C

Exchanger details for T-102B

Heatx results				
Calculation Model: Shortcut				
	Inlet		Outlet	
Hot stream:	STEAM-IN		H2O-OUT	
Temperature:	130	C	118,492	C
Pressure:	1	bar	1	bar
Vapor fraction:	1		1	
1st liquid / Total liquid	1		1	
Cold stream:	PUMP-OUT		REACTOR	
Temperature:	69,8997	C	120	C
Pressure:	6	bar	6	bar
Vapor fraction:	0		0	
1st liquid / Total liquid	1		1	

Exchanger details		
Calculated heat duty:	1,09408e+06	Watt
Required exchanger area:	52,7262	sqm
Actual exchanger area:	52,7262	sqm
Percent over (under) design:	0	
Average U (Dirty):	850	Watt/sqm-K
Average U (Clean):		
UA:	44817,2	J/sec-K
LMTD (Corrected):	24,412	C

Exchanger details for E-102B