

Bachelor Research Project Chemical Engineering

Techno-Economic analysis of large scale Lignin based Rigid
Polyurethane and Epoxy Resin

Written By: Stefan Vasic

Student Number: S3300412

Date: 20/11/2020

Supervisors: Dr. Jos Winkelman, Dr. Peter Dues



university of
groningen

Abstract.

This report investigates two potential high value application of lignin to polymeric materials. The aim was to assess the technical and economic aspects of the chosen applications in order to provide preliminary estimations on cost of up scaling as well as allow a comparison between the two. The two applications of lignin in manufacturing of polymeric materials were chosen as polyurethane and epoxy resin. These two processes were identified based on current market size and growth as well as the current technological standing. Research conducted on the synthesis of such polymeric materials provided the necessary conditions required for production. In addition to this it provided insight into the current limitations of lignin, polyurethanes can be synthesized from lignin without necessary pretreatment but can only effectively replace 30% of the petroleum derived polyol material. Lignin in the production of epoxy resins on the other hand were able to successfully replace the petroleum-derived bisphenol-A but required an extensive depolymerization phase.

Process flow diagrams were constructed to give a clearer depiction of the possible manufacturing process involved in an up scale production. With the use of Aspen plus simulations based on the process flow diagrams could be constructed. A number of issues arose when simulating lignin based manufacturing processes. However simulations of the conventional processes provided insight into the potential production rates. It was found that the total production of polyurethane was 1236.21 kg/hr while the epoxy resin production was found to be 254.3 kg/hr. The large difference is explained by the ability for lignin to only substitute 30% of the petroleum derived polyol. Results obtained from the simulations allowed the development of an economic analysis based on cost estimation curves of equipment's and current prices of materials and utilities. It was found that both polyurethane and the epoxy resin processes would experience a yearly loss of 7.8 million and 11 million USD respectively. However it was concluded that the costs of producing 1 kg of polyurethane foam and epoxy resin stand at 2.32 and 4.5 USD, respectively. The analysis conducted led to the conclusion that application of lignin in the production of polyurethane foams appears to offer greater economical potential than that of epoxy resins. However it should be maintained that while both products currently are not capable of large-scale production, increasing depletion of fossil fuels along with greater environmental concern would inevitably lead to a void in production of polymeric materials. While it is still uncertain on how exactly this void will be filled, it seems most certain that lignin long with other biomaterials will have an integral role to play.

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Introduction.

Petroleum is currently the life source of the chemical industry, with the majority of bulk and fine chemicals being petroleum derived. Bulk chemicals, which include olefins and aromatics like ethylene and benzene are used extensively as starting materials for a variety of essential products. Paints, adhesives, plastics, fertilizers and resins all depend on petroleum-derived compounds. It has become more apparent that petroleum resources are depleting at ever increasing rates. As a result more attention is being aimed at alternative sources of bulk carbon compounds used throughout the chemical industry. While some alternative sources such as vegetable oil, starch and natural rubber are being used in small percentages, greater emphasis has to be placed on finding viable substitutes able to meet the high demand placed on petroleum derived products.

One promising substitute is Lignin, a largely under utilized natural biopolymer found in the cell walls of various cell types in plants and constitutes 20-30% of the weight in wood. Lignin is one of the most abundant biopolymers found in nature with only cellulose and chitin being present in greater quantities. The biopolymer consists of aromatic building blocks called phenylpropanoids, which are present in large quantities. The high quantity of aromatic compounds makes lignin an extremely promising substitute from a chemical point of view. Lignin currently is mainly found as a by-product to the pulp and paper industry, where it is produced in the form of black liquor. Kraft lignin obtained from the paper and pulp industry has an annual production of approximately 50 million tones (Fang and Richard L. Smith). Currently lignin is mainly burnt as low-grade fuel as research on upgrading lignin to specific chemicals through various downstream processes is still ongoing. Due to the abundance and promising structure of lignin more attention has been focused the on extraction and application of this vastly underused biopolymer.

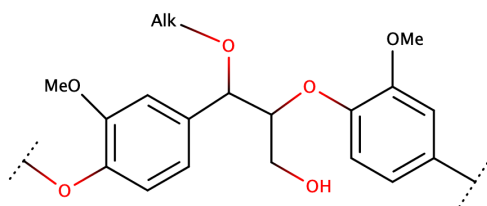


Figure 1: Structure of B-0-4 group (Zijlstra, Analbers and Deuss)

Depending on the extraction method employed the obtained lignin will have differing structures and properties. The most common method of extraction is from the paper and pulp industry, which produces technical lignin known as Kraft lignin, which is extracted through a sulfite process with the use of harsher conditions generating a highly altered lignin derivative. Organosolv extraction proceeds by contacting the lignocellulose biomass with an aqueous organic solvent (most commonly ethanol) in the presence of an acid catalyst, causing the breakdown of lignin and hemicellulose. Low-boiling solvents are often used and are easily retrieved through distillation. The extraction uses milder conditions that allow higher contents of $\beta - 0 - 4$ linkages, thereby preserving the native

structure of lignin (Deuss, Zijlstra and Lahive). The organosolv extraction process is able to produce larger amounts of lignin of higher quality that is relatively pure and unaltered compared to the various other extraction processes (Joaquín Quesada-Medina). The aim of this research is to investigate approaches of lignin application and give an initial economic outlook on each. The applications of lignin are extensive and cannot all possibly be covered in one report. Therefore research conducted will be narrowed to two applications that demonstrate both technical and economic potential. Initially various applications of lignin are considered and two were selected, based on market value and current technical standpoint. Current research details the methods of synthesis required and provided information on materials and conditions necessary to produce both polymeric materials. Through small-scale laboratory experiments and current large scale manufacturing technologies, a process flow diagram detailing a potential large-scale lignin based manufacturing process was constructed. This became the basis for the subsequent simulations and economic analysis. Certain information essential to the construction of a economic analysis such as energy requirements and size estimates of equipment were obtained through simulations of each process with the use of Aspen Plus. The simulations provided all necessary details to carry out the economic analysis and gave an estimation of the best possible outputs obtained from each process.

Application of Lignin.

Developing the production methods of value added products from lignin is crucial in offsetting the high extraction cost affiliated with the organosolv process. Research has been conducted on the potential of lignin as a substitute for petroleum bulk chemicals, in the production of various value added products. Applications such as polyurethane, vanillin, phenolic and epoxy resin have been some of the potential outlooks investigated. The focus of this report is the identification of two possible high value added applications of lignin and subsequent analysis of the technical and economic up scaling of these processes as they currently stand. It should be noted however that the use of Lignin as a substitute for petroleum bulk chemicals currently comes with certain drawbacks. Properties of lignin such as high molecular weight, low reactivity and poor solubility in organic solvent limit its use as a substitute of petroleum derived compounds (Xu and Ferdosian).

Although the applications of lignin are vast there are certain indications as to which may provide greater potential. The presence of phenolic hydroxyl groups within the lignin molecule has conjured interest in its use in the production of certain polymeric products. The application of lignin to polymeric materials with retained physical properties offers great potential in establishing integrated processes able to offset the high extraction costs. Polymeric materials are often highly versatile with a wide range of practical applications.

Certain applications of lignin such as the production of vanillin and phenolic resins have received greater attention in ongoing research. The focus however of this report is on polymeric materials with large market volumes and high value. Although certain specialty products such as vanillin have high value they also

have a low market volume. With the abundance of lignin available it is vital to establish applications of high market volume, which allow the full benefit of lignin to be realized. Polymeric materials in particular are highly versatile with a wide range of practical applications. Currently two main approaches exist in producing lignin based polymeric products. These approaches include initial depolymerization of lignin and subsequent application as well as the direct use of lignin in its polymeric state to yield the desired product (Fang and Richard L. Smith). Therefore in order to cover both of these approaches two appropriate applications of lignin were chosen. As mentioned previously the use of lignin in the production of phenolic resins has been a greater focal point in the ongoing research and therefore it was decided to focus on applications that have received less attention. The two next commonly cited applications of lignin are its use in the production of polyurethane foams and epoxy resin. In order to better understand the demand and production of each polymeric product further information on the market volume was acquired.

The global market of polyurethane reached a value of 37.8 billion USD in 2020 and is expected to increase to a value 53.4 billion USD by 2025 (Markets And Markets). Polyurethane foams correspond to 67% of the total global consumption and are split into two categories classified as rigid or flexible foams based on their physical properties (Gama, Gama and Barros-Timmons). Rigid polyurethane foams are often used as materials for insulation for various construction or refrigeration applications (Grand View Research), while flexible polyurethane foams are used most commonly in the furniture and automotive industry as mattresses and car seats. Rigid polyurethanes in particular have an essential application as an insulating material in the construction industry and represent 25% of the total consumption of polyurethane. Certain countries in particular such as China and India are quickly becoming the largest market for construction, leading to an increase in rigid polyurethane foam production (Hicks and Austin). Restrictions imposed by environmental organizations such as the Environmental Protection Agency have placed pressure on companies to invest into bio-based materials as a substitute for conventional petroleum starting materials (Markets And Markets). Therefore the continual growth of consumption coupled with the focus of finding suitable alternatives could lead to a gap in demand of certain starting materials used in the synthesis of polyurethanes. The main focus of attention has been on finding suitable substitutes for the polyol component in the manufacturing of polyurethane foams.

Epoxy resin on the other hand has a lower global market size of approximately USD 7,9 billion in 2020 with projections estimating a value of USD 9.45 billion by 2025 (Market Data Forecast). The physical properties exhibited by epoxy resins such as resistance to corrosion, high thermal stability and excellent adhesion allow it to exist in a variety of applications found in the coating, paint, adhesion and electronic industries to name a few. Considerable growth is expected in the market of epoxy resin and can be attributed to the increase in demand from automotive, aerospace and wind turbine industries, which are requiring the use of thermoset resins at an increasing rate (Choudhary and Prasad). Much like polyurethane foams, greater environmental concerns in the manufacturing of

epoxy resins has led to an increased interest in the pursuit of bio-based alternatives. The conventional production of epoxy resin produces high amounts of carbon monoxide and carbon dioxide along with various other compounds. The production of toxic gasses along with the non-biodegradable property has led to the increase search of bio-based reactants. Polyurethane as well as epoxy resin demonstrate high market consumption due to their vast industrial applications. Increase in environmental concerns as well as market size creates a unique opportunity for the application of lignin in the production of high value polymeric products. Two high value applications of lignin were selected based on current market values and expected growth. It is expected that direct up-scale of laboratory experiments will most likely produce a deficit in yearly income. Therefore focus on polymeric products with indispensable applications and estimated growth provides the greatest possibility for future large-scale production.

Theory.

The following section provides background information of the synthesis of polyurethane and epoxy resins as well as the current methods employed in producing lignin-based polyurethane and epoxy resins. In addition to this limitations in the use of lignin are discussed through comparisons of conventional and lignin derived polymeric products.

Polyurethane:

Polyurethanes are formed through a step-growth polymerization reaction between a diisocyanate and a polyol, which result in the formation of urethane linkages as shown in figure 2. As mentioned previously the presence of aliphatic and phenolic hydroxyl groups in the molecular structure of lignin allows it to act as a polyol like material, with limitations being present however on the amount of lignin able to substitute conventional polyols. Due to the rigid molecular structure of lignin high concentrations lead to extremely brittle and rigid polyurethanes that offer no practical use (Yasuyuki).

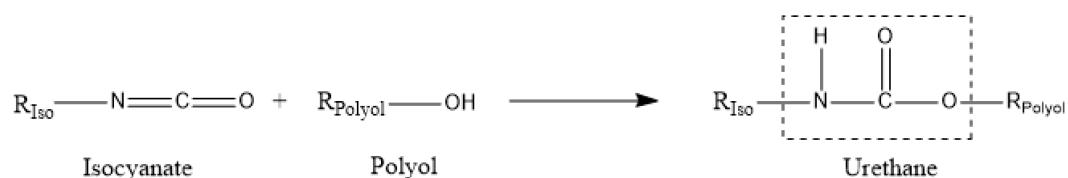


Figure 2: General reaction urethane formation

The use of lignin in the preparation of polyurethane foams proceeds through either the direct use of lignin or an initial pretreatment step followed by the ensuing polymerization reaction. Pretreatment methods of lignin often involve chain extension reactions of lignin with propylene oxide, with the aim of converting the lignin into a liquid polyol while increasing hydroxyl content and reactivity of the lignin polyol. Studies conducted by (Cateto, Barreiro and

Rodrigues) and (Nadji, Bruzzese and Belgacem) carried out the oxypropylation of various lignins in the presence of potassium hydroxide acting as a catalyst. Both studies demonstrated an increase in the hydroxyl index of the ensuing organosolv lignins reaching index values in the range of 200-300 mg KOH/g Lignin, which are values similar to polyols used in industry. In addition to this however the molecular weights of the oxypropylated lignins had significantly increased from values of 700 to 2500 g/mol for organosolv lignin. The incorporation of propylene oxide resulted in increased viscosity of the lignins, with values increasing as ratio of lignin-propylene oxide increased. The viscosity of polyol used is critical in the formation of polyurethane foams, high viscosity polyols can result in poor mixing of reactants leading to an uneven distribution of bubbles formed in the cell structure from reactions of the blowing agent and diisocyanate. Although the oxypropylation of lignin does seem to improve the hydroxyl index and therefore could possibly give rise to greater reactivity of the hydroxyl groups, further research is required in investigating the extent to which oxypropylation pretreatments aid in the production of the ensuing polyurethane foams.

Lignin however has also been employed as a polyol without any prior treatment; the direct use of lignin in the production of polyurethanes conducted by (Pan and Saddler) compared the use of kraft and organosolv lignins as direct substitutes for conventional polyols used. The effect of varying the concentration of lignin substituting the petroleum-derived polyol was investigated through varying the molar percentage of substituted lignin between 25-70 percent. The organosolv lignin used had a higher molecular weight and lower aliphatic and phenolic hydroxyl content than that of the kraft lignin, it was therefore initially expected that the kraft lignin would produce polyurethanes of better thermal and physical properties. However upon blending the lignins with the petroleum based polyether polyol it was found that the kraft lignin led to a dramatic increase in the viscosity of the solution. This was attributed to the poor solubility of the kraft lignin in the polyether polyol, for example at lignin concentrations of 40 wt.% the viscosity of the organosolv lignin-polyol solution was found to be 6000 $mPa \cdot s$ while the kraft lignin-polyol solution reached values of over 16000 $mPa \cdot s$. This is most likely caused by the retained native structure of organosolv lignin, which displays far better solubility in organic solvents than the kraft lignin, which was found to be insoluble in alcohols and therefore was only suspended in the polyol solution. The increase solubility of organosolv lignin led to polyurethanes with greater values of compressive strength and density than the kraft lignin derived polyurethanes. The highest values of compressive strength were found at concentrations of lignin at only 25 wt.%, at this composition the compressive strength of the organosolv polyurethane had values of 0.3 MPa while the kraft lignin polyurethane foams produced values of approximately 0.2 MPa. It should be noted however that there is a significant decrease in both the compressive strength and density of lignin polyurethanes compared to that of conventional petroleum based polyurethanes. This can be seen particularly in the compressive strength values obtained which indicate a 40% reduction when lignin concentration reaches 25 wt.% (Pan and Saddler). Therefore it has to be understood that while organosolv lignin does prove to produce polyurethanes with better physical properties than that of kraft lignin, the general inclusion of

lignin in cell structure of the foam causes a decrease in physical properties most likely caused by the bulky structure of lignin leading to less regular cell formation. Nevertheless it was concluded that at organosolv lignin contents of 25-30 wt.% the polyurethane foams produced had a satisfactory structure and physical properties, without the use of pretreatment methods. Therefore the use of organosolv lignin in particular offers the greatest potential in providing a legitimate substitute to the petroleum based polyols but certainly requires greater research into further improving the properties of the produced polyurethanes.

Studies conducted by (Emanuele, Ferri and Bonini) and (Ni and Thring) demonstrate methods of synthesizing lignin-based polyurethane. The methods used often employ THF as a solvent acting to dissolve the lignin along with the diisocyanate. The choice of polyol is also vital in the production of polyurethanes; most noticeably polyethylene glycol is the choice of polyol. One study conducted by (Thring and Vanderlaan) investigated the use of polyethylene glycol with differing molecular weights of 400, 1000 and 1500 g/mol. The study concluded that less of the lignin structure was incorporated into the polyurethane matrix when PEG of molecular weights 1000 and 1500 were used. Therefore it was shown that the use of PEG400 works better as a polyol for the production of lignin based polyurethanes. The various studies mentioned conducted the polymerization reaction at temperatures ranging from 60-72°C. The choice of temperature ultimately depends on various other parameters such the presence of a catalyst during the polymerization reaction. In addition to this the residence times of the polymerization were found to be in the range of 40 minutes to one hour. The characterization of the lignin-based polyurethane led to the conclusion that at lignin contents above 30% the obtained polyurethanes were brittle and hard (Thring and Vanderlaan). Therefore this again confirms that the amount of lignin able to effectively replace the petroleum polyol is limited to around 30%.

Epoxy resin:

The formation of epoxy resin like that of polyurethane is formed through a step-growth polymerization reaction most commonly between epichlorohydrin and bisphenol-A in the presence of an alkaline catalyst. The reaction causes the bonding of the epoxy group to each end of the diol creating a polymer with the structure as seen in figure 3. The use of lignin as a substitute to bisphenol-A has been the subject of ongoing research; focusing on the preparation of epoxy resins through firstly the initial depolymerization of lignin and subsequent epoxidation.

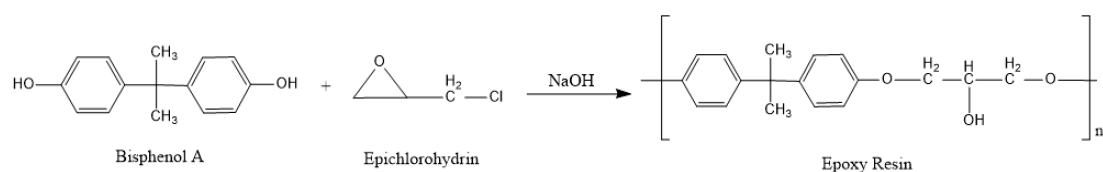


Figure 3: General reaction of epoxy resin

Studies conducted with the direct use of lignin as a starting material in the epoxidation reaction produced epoxy resins with high molecular weight, which were found to be insufficient in applications of epoxy resins. Therefore chemical

modification of lignin prior to epoxidation seems to be a more promising method of synthesis. A common method found in research is the initial depolymerization of lignin, which has shown through studies to reduce molecular weight and polydispersity. One study conducted by (Ferdosian and Yuan) synthesized lignin based epoxy resins from depolymerized organosolv lignin. The depolymerization of the organosolv lignin led to a decrease in molecular weight from 2638 g/mol to 986 g/mol, while the polydispersity of the polymer was also decreased from 3.58 to 2.37 demonstrating a more narrow molecular weight distribution of the depolymerized lignin. Another study carried out by (Fatemeh and Mark) concluded that the depolymerization of organosolv lignin lead as well to an increase in the hydroxyl group content which greatly increases the reactivity of the lignin in the subsequent epoxidation reaction. Characterization of the lignin-based epoxy resins were carried out with the use of FTIR spectroscopy, the results concluded the presence of the epoxy functionalities on the epoxidized depolymerized organosolv lignin. In addition to this thermal properties of the epoxidized lignin were investigated through differential scanning calorimetry, the lignin epoxy resin demonstrated greater thermal stability compared to that of the depolymerized lignin. It was concluded that this was caused by cross-linking induced by the presence of epoxy groups, thereby demonstrating the successful grafting of epoxy groups onto the structure of lignin. In summary, while the synthesis of lignin-based polyurethanes can occur with the direct use of organosolv lignin to yield polyurethanes with sufficient physical properties. The direct use of organosolv lignin in the synthesis of epoxy resins leads to high molecular weight of epoxy resins which are not suitable for many applications, therefore the synthesis of lignin-based epoxy resin require an initial depolymerization step, which decreases the molecular weight while simultaneously increasing total hydroxyl content. Thereby increasing reactivity of the organosolv lignin, which should ultimately lead to a higher yield of lignin-based epoxy formed.

Both studies (Fatemeh and Mark) and (Ferdosian and Yuan) presented the methodology behind the production of lignin based epoxy resin. Firstly the depolymerization of the organosolv lignin took place, which began by adding 50 grams organosolv lignin, 2 grams ruthenium on carbon catalyst and 150-gram acetone in a stirred autoclave reactor. The reactor was then pressurized to 100 bar with the use of hydrogen. The reactor was then heated to 350°C and for one hour to allow the depolymerization to occur. The gaseous and liquid products were then separated and the acetone removed with the use of a rotary evaporator at 50°C, with yields of depolymerized lignin being recorded at 85%. The epoxidation of the depolymerized lignin was carried out at various operating conditions to determine most effective method of production. Variables such as residence time, epichlorohydrin (ECH)/lignin ratio, sodium hydroxide/lignin ratio and temperature were varied to determine the optimum conditions. It was found that higher ratios of epichlorohydrin to lignin gave higher yields of product; in addition to this greater yields of product were obtained when reaction times were increased from 3 to 5 hours. Both of the studies mentioned were able to conclude that the high product yields were obtained at high ECH/lignin ratios of 4 with a residence time of 5 hours at temperatures of 70°C.

The results concluded by (Ferdosian and Yuan) became the basis of the conditions necessary in the depolymerization and epoxidation of lignin.

Manufacturing Process.

The previous section detailed the current technical aspects of synthesizing lignin based polyurethane and epoxy resin. The current section provides information regarding the current methods and technologies employed in the manufacturing of polyurethanes and epoxy resin while incorporating information provided in the previous section to construct the preliminary block diagrams of each process.

Polyurethane:

The conventional manufacturing process of polyurethanes is rather straightforward and can be broken down into distinct phases of production. Firstly the reactants involved which include mostly the diisocyanate, polyol and blowing agent are held as liquids in large continuously stirred storage tanks, which ensure the reactants remain in the liquid phase. Through the use of various control devices the mixture of reactants is pumped out of the storage tank in the appropriate amount where it enters into the tube side of a heat exchanger. The temperature of the heat exchanger is adjusted then to a high enough temperature to allow the polymerization reaction to occur; typically a temperature of 70°C is used.

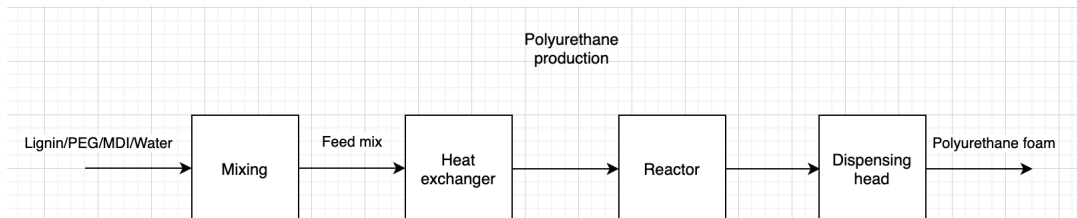


Figure 4: Block diagram polyurethane process

The heating of the reaction mixture induces the polymerization reaction where the polyurethane is then formed. Depending on the formulation and desired application of the polyurethane foam various different technologies can be employed. In the production of rigid polyurethane foams most often requires the use of dispensing heads, which once the polymerization is complete spray the polyurethane formula onto a conveyor belt that allows sheets of polyurethane foam to form. Other methods used directly inject the polyurethane formulation into a mold where the foam will expand due to the reaction of the isocyanate and the blowing agent creating carbon dioxide, filling the cavity and creating the desired shape for application. Therefore as there is a wide variety of processing technologies the focus of the manufacturing of lignin-based polyurethanes will be on the manufacturing steps needed for the polymerization to occur. An overall block diagram of the manufacturing process is shown in figure 4.

The functionality of the heat exchanger is divided to give a clearer description of the process and allow for later simulations to be made. Therefore in the block diagram shown in figure 4 the heat exchanger acts solely to increase the

temperature of the solution before it passes into the reactor where polymerization occurs. One of the key differences in the formulation of lignin-based polyurethanes is the use of organic solvent most commonly THF, which is used to initially solubilize the lignin and di-isocyanate before being passed through to the heat exchanger and subsequently the reactor. The same procedure occurs for PEG400, which is also solubilized in THF before proceeding into the reactor. Once the appropriate time has elapsed the now formed polyurethane can pass through to the dispensing heads where the solution can be sprayed onto a conveyor belt allowing the foam to rise.

Epoxy Resin:

The process involved in the production of lignin-based epoxy resin is somewhat more complex as an initial depolymerization phase is required. The overall depolymerization phase is shown as a pretreatment step in the block diagram shown in figure 5. Greater description of the depolymerization can be found in the process flow diagram section of the report. Following the depolymerization is the separation of depolymerized lignin. This occurs firstly through the separation of liquid product containing the depolymerized lignin, which then passes through to a filtration stage where the ruthenium on carbon catalyst is separated from the liquid solution. The final stage in the depolymerization of lignin is the removal of acetone through the use of an evaporator, thereby yielding the depolymerized lignin.

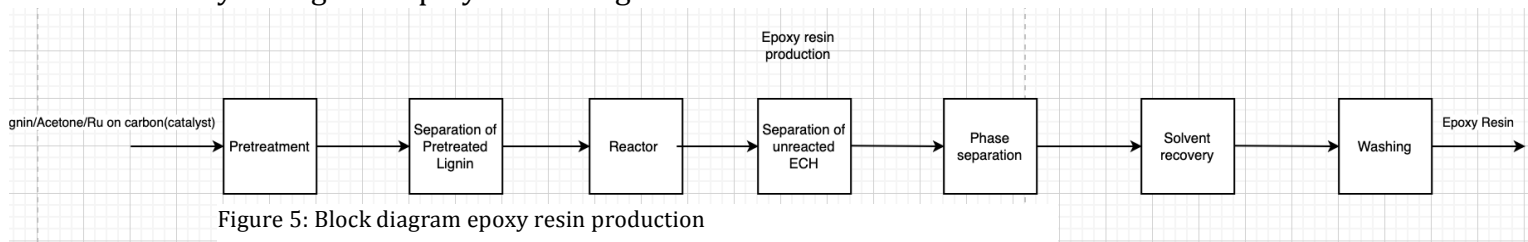


Figure 5: Block diagram epoxy resin production

The now de-polymerized lignin is passed into a reactor along with the caustic soda solution and epichlorohydrin, where the polymerization reaction will occur. Depending on the temperature during the reaction either a liquid or solid epoxy resin is formed, higher temperatures above 80°C lead to the formation of solid epoxy resins and can possibly plug the reactor (Chang and Shirtum). After the polymerization is complete the excess epichlorohydrin is separated from the solution with the use of an evaporator. Through the use of adequate solvents such as MIBK the organic phase epoxy resin can be separated from the caustic solution. The solvent is then often evaporated from the epoxy resin, which then enters into a washing stage where preferably distillate water is used. Lastly the resin is dried to allow the removal of water and the final product is obtained.

Process Flow Diagram.

The more detailed process flow diagrams of each process are shown and described in this section, which provide the basis for subsequent simulations and economic analysis.

Lignin based Polyurethane:

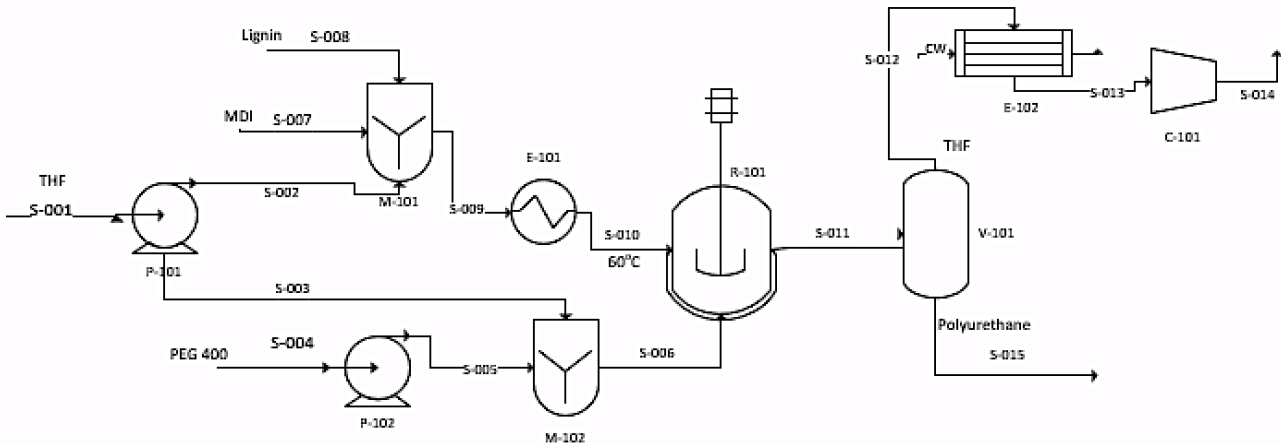


Figure 6: PFD Lignin based polyurethane

The process flow diagram for the preparation of lignin-polyurethanes is shown in figure 6. The first step in the production of polyurethanes consists of dissolving the lignin, methylene diphenyl diisocyanate and the polyethylene glycol in THF. The lignin and diisocyanate are placed into mixer M-101 where they are dissolved separately from the polyol. In the preparation of lignin-based polyurethanes reactants such as the conventional polyol or diisocyanate are often mixed with the lignin separately or added at a later stage to ensure adequate mixing of lignin and polyol or diisocyanate component, which ensures the forming of a consistent pre-polymerization mixture. The solubilized solution of lignin and MDI is then charged into heater E-101 where the temperature of the solution is increased to 60°C before being discharged into the reactor. The polyethylene glycol is initially also solubilized in THF in the separate mixer M-102 and then subsequently added to the reactor. The polyol mixture along with the lignin-diisocyanate mixture then reacts forming urethane groups from both the lignin and polyol. This allows the formation of a polyurethane polymer network that includes both the polyol and lignin. Once the polymerization is complete the solvent THF is then removed through the use of an evaporator V-101. Depending on the application of the polyurethane the remaining lignin-polyurethane solution is either dispensed onto a conveyor belt or injection molded into a cast to meet a desired specification of dimension.

Lignin based Epoxy Resin:

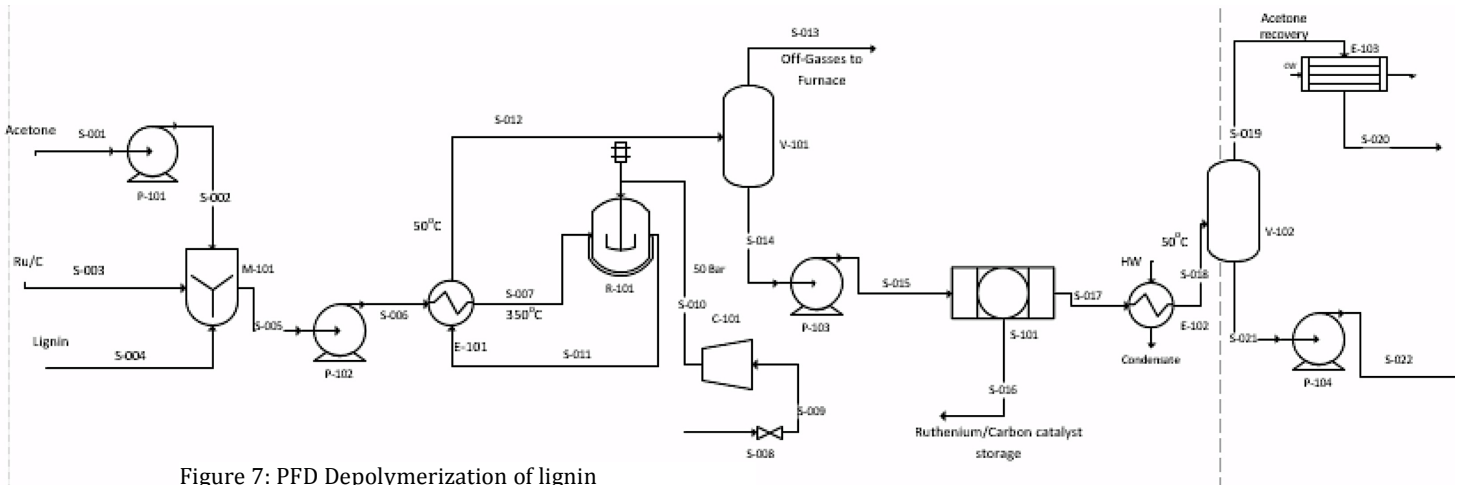


Figure 7: PFD Depolymerization of lignin

The process of synthesis for lignin-based epoxy resins can be split into two distinct stages. The initial depolymerization of the lignin followed by the subsequent polymerization to form the corresponding epoxy resin. For the sake of clarity the two stages are shown separately, but would most likely be one continuous process. The full PFD of the joined epoxy resin process is shown in Appendix A. The PFD of the depolymerization of lignin is shown in figure 7, the first step consists of mixing the lignin along with the catalyst ruthenium on carbon and the solvent acetone in mixer M-101. The solution is then pumped into heat exchanger E-101 where the temperature of the solution is raised to 350°C, before entering into reactor R-101. Hydrogen is pressurized with the use of compressor C-101, which increases the pressure to 100 bar before entering the reactor. The depolymerization occurs for approximately one hour after which the depolymerized lignin solution is cooled with the use of heat exchanger E-101. The depolymerized solution is able to act as a heating medium for the incoming reactor feed, allowing greater heat integration within the process. The depolymerized solution is now cooled to a sufficiently lower temperature. Existing alongside the solution is a gaseous phase that is comprised of mainly H₂, CH₄, CO₂, C₂H₆ and C₃H₈ that are then separated with the use of distillation column V-101. The liquid distillate is then transported through a filter collecting the ruthenium on carbon catalyst, which is then recycled through the process. The last step in the depolymerization stage is the removal of acetone as a solvent from the depolymerized lignin. Firstly however the solution is heated with the use of E-102, which heats the solution to 50°C before the solution, enters evaporator V-102. The recovered acetone, which leaves through pipeline S-019 is condensed and recycled back through the process. The bottom stream contains the pure depolymerized lignin, which is then subsequently used in the production of lignin based epoxy resin.

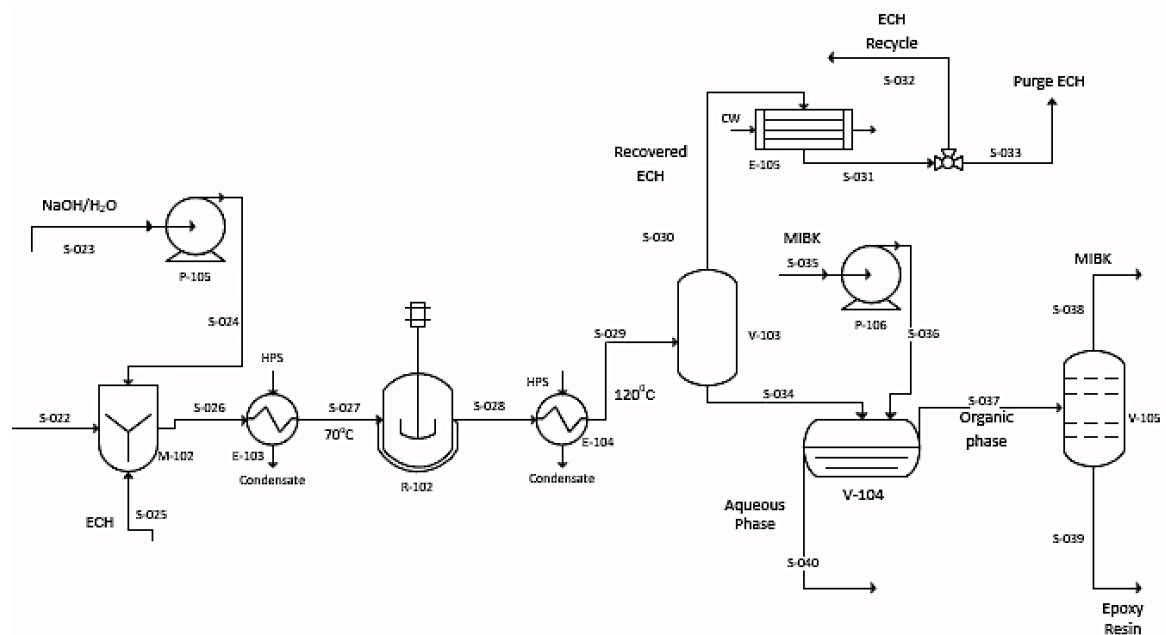


Figure 8: PFD lignin based epoxy resin

The initial step in the production of lignin-based epoxy resins is mixing of the reactants in mixer M-102, which combines the depolymerized lignin, epichlorohydrin and sodium hydroxide solution. The solution is then transferred to heater E-103, which increases the temperature of the mixture to 70°C. The mixture is then subsequently charged into reactor R-102, where the polymerization takes place. The reaction continues for a time of approximately 5 hours, once the polymerization is complete the solution of lignin based epoxy is then heated once more to a temperature of 120°C. The increase in temperature is necessary to recover the unreacted epichlorohydrin, which is added in excess, the unreacted epichlorohydrin is recovered through the use of evaporator V-103. The recovered epichlorohydrin then passes through condenser E-105 with the majority of the epichlorohydrin being recycled back through the process. A purge of the recovered epichlorohydrin is also in place to ensure that there is no accumulation within the process. The remaining solution, which consists of the lignin-based epoxy resin, as well as the sodium hydroxide solution exits from stream S-034 and enters a decanter labeled V-104. The inert solvent MIBK enters the decanter to aid in the phase separation. The aqueous phase, which consists of the sodium hydroxide solution, exits the bottom of the decanter while the organic phases, which consist of the MIBK and lignin-based epoxy resin, are transported for further processing. Finally the MIBK solvent is removed with the use of an evaporator at temperatures of 115°C. The final lignin based epoxy product then proceeds to subsequent washing and drying stages.

Process Modeling.

The processes of lignin based polyurethane and epoxy resin were simulated with the use of Aspen Plus, software often used in modeling various different chemical processes. A variety of unit operations can be modeled with the use of Aspen, which utilizes thermodynamic property data allowing calculation for both the pure components involved in the reaction as well as binary interactions between components. A key aspect is the choices of method used to determine the thermodynamic properties of various components. In order to successfully model an operation the appropriate method of calculation or property package has to be chosen. Aspen has a wide variety of property packages, which allow the modeling of vast number of processes. The key thermodynamic property used within the calculations of Aspen is phase equilibrium. Within Aspen exist two categories of phase equilibrium calculations that are defined as equation of state and activity coefficient methods. The choice of which method is used to calculate phase equilibrium greatly impacts the calculations of all other thermodynamic properties such as molar volume and enthalpy. Depending on whether polar or non-polar components are used and the operating conditions of the process, the appropriate property package is selected. With the use of flow charts obtained from (Carlson) an accurate initial assessment on the required physical property method can be made. Modeling processes involving lignin however does pose a challenge, as the biopolymer is not in any of the databanks of Aspen. Therefore the physical properties of lignin are not present and have to be either entered manually from experimental data or estimated with the use of the NIST function within Aspen, however the structure of lignin still needs to be defined in order for the simulation to run successfully. Particularly since lignin is a major component with the process and greatly influences the structure of products formed.

Estimation of thermodynamic properties of polar components is best done with the use of activity coefficient property packages such as UNIFAC, which use a group contribution method to calculate properties such as normal boiling point, ideal heat capacity and critical pressure. Estimation of these parameters however should be used cautiously within Aspen and the limitations of these calculations need to be carefully understood. For example certain parameters such as the fugacity of the component are calculated in Aspen with the use of the Antoine equation. The coefficients needed cannot be estimated from a user-defined structure drawn In Aspen. Therefore these parameters along with many others should be obtained through experimental data, or estimated from similar components. It should be noted however that this substantially affects the accuracy of the simulated process. Therefore as lignin was not present in Aspen databanks, user defined structures would need to be inputted into Aspen. The lack of a definite structure and experimental data on binary interactions of lignin make the simulation of lignin difficult and very inaccurate. Therefore the simulations of both polyurethane and epoxy resin were carried out with the use of conventional starting materials which were mostly present in Aspen databanks or had simple structures that allowed parameters to be estimated with greater ease.

Polyurethane:

Firstly when starting the simulation an appropriate property package for the polyurethane process would be selected. As the process involves polar components, which do not form an electrolyte solution with pressures lower than 10 bar the most suitable property package was shown to be UNIFAC (Carlson). The full diagram of the simulated polyurethane process can be seen in figure 9, initially the amounts of lignin polyurethane, PEG400 and THF were determined.

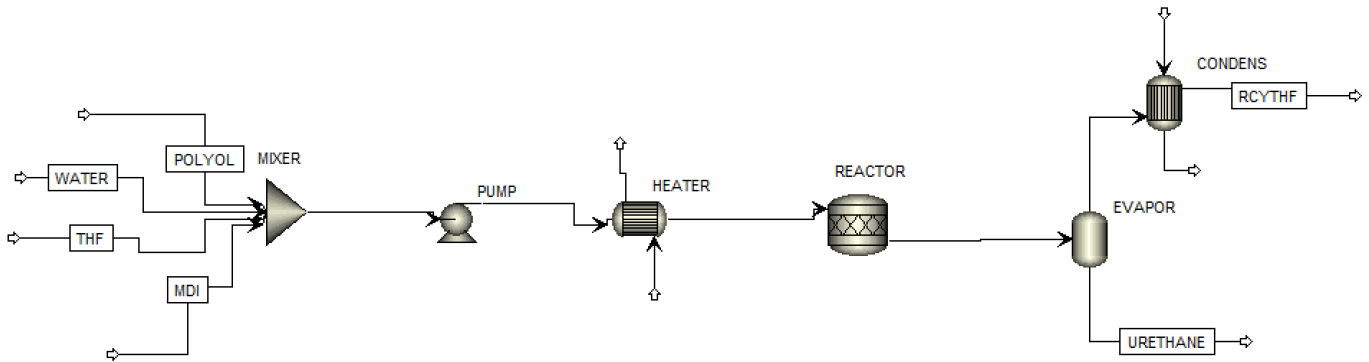


Figure 9: Aspen simulation of lignin polyurethane

From research conducted by (Herry) on large-scale organosolv extraction it was found that at extraction times of 3 hours the highest yield of lignin obtained was 1.353 tones. Therefore an optimum initial input of lignin was calculated as 451 kg/hour, which was halved exactly to ensure that both the polyurethane and epoxy process began with the same initial amount of lignin. Therefore an initial input of 225,5 kg of lignin was used as the starting material for the polyurethane process. As the amount of lignin used within the process is limited to 30 wt.% the remaining proportion was filled with 526 kg of PEG400. The amount of MDI needed in the process can be calculated with the use of equation 1. Where the term “W” denotes the weight in grams of the compound while [NCO] and [OH] is the corresponding molar contents of isocyanate and hydroxyl groups respectively.

$$\frac{NCO}{OH} = \frac{W_{MDI} \cdot [NCO]_{MDI}}{W_L \cdot [OH]_L + W_{PEG} \cdot [OH]_{PEG}} \quad Eq. 1$$

Calculations were carried out with data acquired from (Ni and Thring) and (Pan and Saddler), in addition an NCO/OH ratio of 1.1 was used which is common in the production of rigid polyurethane foams. The calculation resulted in an inlet feed of methylene diphenyl diisocyanate of 536.5 kg. In addition roughly 10% of water was used as the blowing agent, which resulted in a water flow rate of 0.141 m³ per hour, which equates to 140.6 kg/hour. The results of the simulation revealed that the total production of polyurethane was 1236,21 kg/hour. Taking

a yearly operational time of 8000 hours reveals that the total amount of polyurethane produced is 9.8 kilo tones per year, a value which is consistent with amounts of polyurethane produced in existing production plants.

Epoxy Resin:

The depolymerization process was modeled as seen in figure 10. The amount of acetone and ruthenium on carbon required were taken from experiments conducted by (Ferdosian and Yuan) and up-scaled to values where the initial lignin input is 225.5 kg. This led to a feed inlet of 676.5 kg of acetone and 9.02 kg of ruthenium on carbon catalyst. This was then fed into the reactor, which was pressurized to 100 bar with the use of hydrogen. The depolymerization reaction itself was not simulated due to the unknown structure of lignin and lack of experimental data. Therefore bisphenol-A was taken in the same weight and simulated through the reactor, which maintained the same operating conditions as to that of the laboratory experiments conducted. This allowed the relative utilities of each piece of equipment to be calculated allowing for a more accurate economic analysis of the process. One compound that was not present within the Aspen databanks was ruthenium on carbon, instead however a separate ruthenium catalyst, ruthenocene in the same amounts was used and classified as a solid within Aspen. This allowed relevant information on solid equipment such as the filter used to recover the catalyst after depolymerization to be collected and included in the later economic analysis. Once the catalyst has been filtered and the acetone evaporated the depolymerized lignin flows through to the next stage of epoxidation.

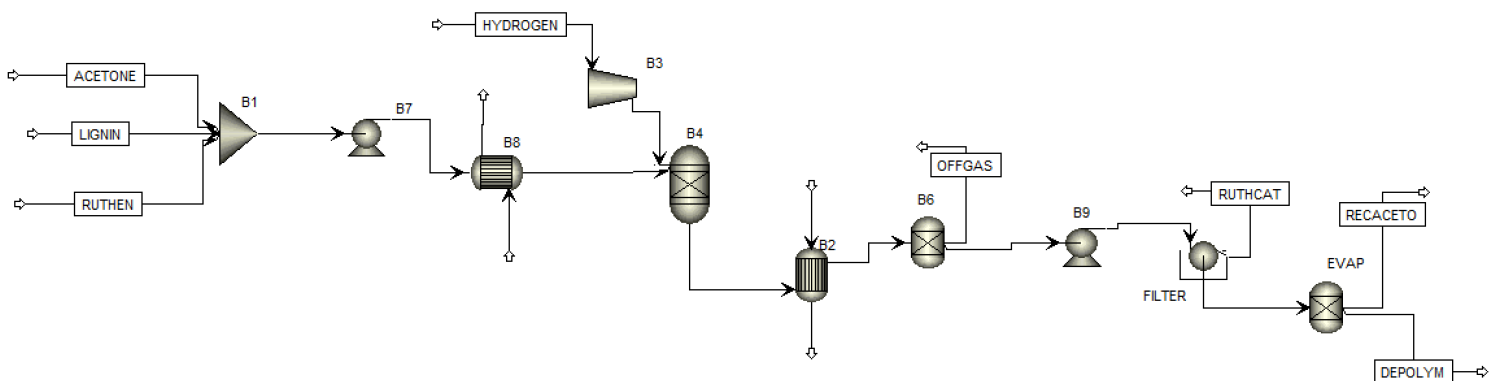


Figure 10: Aspen simulation lignin depolymerization

The modeling of the epoxidation process is shown in figure 11. Although the depolymerization and epoxidation process are shown separately it is most likely that these would be sequential steps in the preparation of lignin-based epoxy resins. The first step in the epoxidation process is mixing of the depolymerized lignin with 84.638 kg of epichlorohydrin and 27.442 kg of sodium hydroxide solution. The now mixed feed is then again transported to the reactor where the epoxidation process is carried out at 70°C. The remaining steps of the process are simulated as described in the process flow diagram. It should be noted that the separators used to separate the solvents and phases of the epoxy solution are component separators that use split fractions of specific components and allow

the complete separation of epoxy from the solvents. The final separator used however was set as a distillation column; with the necessary temperatures required for separation determined through binary analysis of the MIBK and the epoxy resin. Although the structure of the epoxy resin is different to that of the lignin-based epoxy, the use of Aspen binary analysis can provide accurate information on conditions required for the separation between lignin-epoxy resin and solvents, provided the correct structure and properties are known. The final obtained lignin-based epoxy resin has a mass flow rate of 254.3 kg/hr.

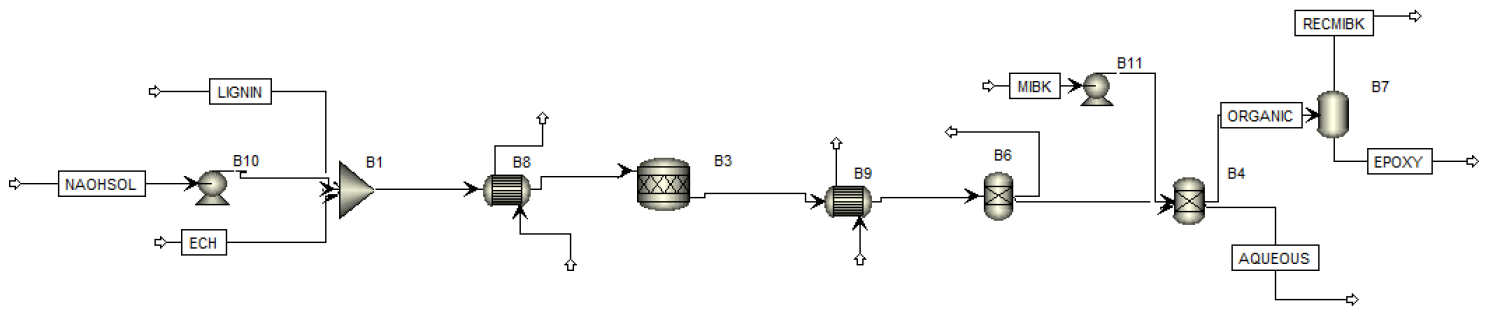


Figure 11: Aspen simulation lignin epoxy resin

The simulation of each process through the use of Aspen Plus allowed for the subsequent economic analysis to be established. Estimations of equipment size and various other parameters required for the economic analysis can be obtained with the use of Aspen Economic Analyzer function. Individual sizing of each piece of equipment can be completed within Aspen Plus and would provide a more accurate assessment. Nevertheless the Economic Analyzer does produce reasonable estimates based on the operating conditions and flow rates used throughout the simulation.

Economic Analysis.

The various sub-sections of this report provided necessary information for the constructed of a preliminary economic analysis. In order to determine the feasibility of each process an economic analysis was conducted, which provides a preliminary insight into the costs of investment and operation of the proposed manufacturing processes. The cost analysis was conducted with the use of (Towler and Sinnott). The fixed capital investment, which covers the costs required for designing, constructing and installing the manufacturing plant as well as any additional costs necessary to prepare the plant site. The fixed capital investment is comprised of ISBL, OSBL, engineering and contingency costs. Firstly the ISBL costs refer to all costs required to obtain and install all necessary equipment for the process. The OSBL or offsite costs are expenses due to modifications of the sites infrastructure. Modifications are often required to account for the capacity needs of the manufacturing process, which involves the supply of utilities such as electricity and water. The design and engineering costs represent the costs of designing the process plant as well as additional engineering costs. Finally the contingency costs are set in place to allow some variation from the estimated costs and to ensure that the budget for the project is sufficient. Firstly in order to estimate the costs of equipment, the following equation is used which is obtained from (Towler and Sinnott).

$$C_{Equip} = a + b \cdot S^n \text{ Eq. 2}$$

The values of “a” and “b” are the cost constants while “S” is the sizing parameter for the specific type of equipment used, lastly the exponent “n” is a factor specific to the piece of equipment used. The sizing parameters for each piece of equipment were obtained through estimations produced by Aspen. The installment costs associated with installing the equipment was estimated with the use of the Lang factor, which for a mixed fluids and solid processing plant was taken as a value of 3.63. This gave the total ISBL fixed capital costs and allowed subsequent estimation of the OSBL, engineering and contingency costs. The results obtained from the costs analysis can be seen in table 1.

	Polyurethane	Epoxy resin
ISBL	1.16 Mega USD	11.9 Mega USD
OSBL	0.464 Mega USD	4.74 Mega USD
D&E	0.325 Mega USD	3.32 Mega USD
Contingency	0.406 Mega USD	4.15 Mega USD
Fixed Capital	2.35 Mega USD	24.1 Mega USD

Table 1: Fixed capital costs of Polyurethane and Epoxy processes

As shown in table 1 the fixed capital investment required to set up a polyurethane manufacturing process is substantially lower than that of the epoxy resin process. This is of course due to the greater number of equipment pieces needed to carry out the depolymerization of lignin as a pre-treatment step in the production of epoxy resin. The cost of materials as well as utilities required were then calculated with the results shown in table 2. It is clear that although the fixed capital investment of the polyurethane process is sufficiently lower than that of epoxy resin, the high cost of material leads to annual costs substantially higher than that of epoxy resin. This caused by the high volumes of THF solvent and PEG400 required. The utility costs are understandably higher for the epoxy resin process as the amount of equipment required is far greater.

	Epoxy Resin	Polyurethane
Material Cost	18.6 Mega USD	24.5 Mega USD
Utility Cost	1.57 Mega USD	0.266 Mega USD
Yearly Cost	20.2 Mega USD	24.8 Mega USD

Table 2: Yearly costs summary

Finally the total yearly income of each process could be determined, the price of polyurethane per kilogram was found to be 2.32 USD. While for epoxy resin the price per kilogram was found at values of 4.5 USD. Utilizing the values of yearly expenditure on materials and utility allowed the annual income of both processes to be calculated which are shown in table 3. It is clear that while the price per kilogram of epoxy resin is higher, the sheer volume of polyurethane produced gives a larger annual income.

	Epoxy	Polyurethane
Price/kg	4,5 USD	2,32 USD
Output- kg/hour	254,28	917,629 US
Yearly Output (kg)	2034240	7341032
Income	9.15 Mega USD	17 Mega USD
Cost/kg	9,91 USD	3,38 USD

Table 3: Annual earnings

This however is not the best representation as the large amount of the polyurethane product formed is not a reflection of the efficiency of the process but rather that lignin can only effectively replace 30 wt.% of the polyol. Both of the processes regardless of output are in a clear deficit as the price of each product currently stands. The polyurethane process is in a yearly deficit of 7.8 million USD, while the epoxy resin production has an even larger deficit of 11 million USD. It was expected that these processes would not be initially estimated as profitable, nevertheless it is clear that the polyurethane production demonstrates a greater potential in turning a profit. To confirm this belief the cost per kilogram of product was calculated and it was found that the cost of producing 1 kilogram of lignin based epoxy resin amounted to 9.9 USD while the

cost of producing 1 kilogram of polyurethane came to a price of 3.4 USD. The differences in costs are not drastic when considering the scale of operation. However it is evident that the polyurethane process offers a better opportunity in successfully manufacturing a lignin based polymeric material. It should be noted however that these estimates still have a large degree of inaccuracy and that if more accurate estimations are to be made, the sizing of equipment and general design of each plant has to be further developed. In addition to this one area of interest would be to compare the cost of the polyurethane process when an effective pretreatment method is in place. The cost analysis indicates the high costs of establishing pre treatment of lignin. While the thermal and physical properties of certain lignin-based polyurethanes are of sufficient standard, far greater research is necessary in order to ensure that the products are able to meet required standards based on application. The same could be said for the formation of epoxy resins, while the technology is available and pretreatment methods as well as epoxidation techniques have successfully been demonstrated, economic viability of such an operation is still questionable. It seems apparent that the effect of adding a pretreatment stage to the process drastically increased costs of production, more specific information on the costs associated with the depolymerization of epoxy resin can be found in Appendix B.2. It seems most likely that an initial stage of pretreatment would be required in order to produce lignin based polymeric materials. Therefore cost effective pretreatment methods are necessary if effective polymeric products are to be produced from lignin.

Conclusion.

The research project aimed to investigate two potential high value applications of lignin. The production of polymeric materials from lignin offers possibly the best advantage in the manufacturing of products that are able to offset high extraction costs. Through market and technical research the two potential applications of lignin, polyurethane and epoxy resin were identified. Current research has demonstrated the effective production of both lignin-based polyurethanes and epoxy resins; with either a complete substitution of petroleum derived products or only partial substitution. In addition to this depending on the polymeric product various pretreatment methods can be used which greatly enhances the properties of lignin. Process flow diagrams were constructed which gave an insight into the potential upscale manufacturing of lignin based polymeric materials. Simulations of the processes provided a preliminary insight into the production scale and expected outputs from such applications. With a total lignin based polyurethane production rate of 1236.21 kg/hour and an epoxy resin production of 254.3 kg/hour. Each section within the report provided information necessary in order to construct the process flow diagrams and subsequent simulations to provide the required data necessary to produce a preliminary economic analysis. The economic analysis conducted gave insight into the profitability of the lignin based polymeric processes.

While it was concluded that both processes are not currently as it stands able to generate profit. This was somewhat expected as research of the use of lignin is still ongoing. It was revealed however that polyurethane when no pretreatment is required provides better opportunity in offsetting the high costs of materials. This was shown through the cost of production per kilogram of product, which was calculated as 9.9 USD and 3.4 USD for epoxy resin and polyurethane respectively. The fact that the processes do not turn a profit currently should be no indication of future prospects; the reality is that petroleum resources will eventually be depleted, creating a high demand for bio-based alternatives. Lignin possesses the ability to produce polymeric materials that have vital applications in a number of industries. Therefore any current estimations on the up scaling of such processes should serve more as an indication of how much further progress is required before such large scale applications can be realized.

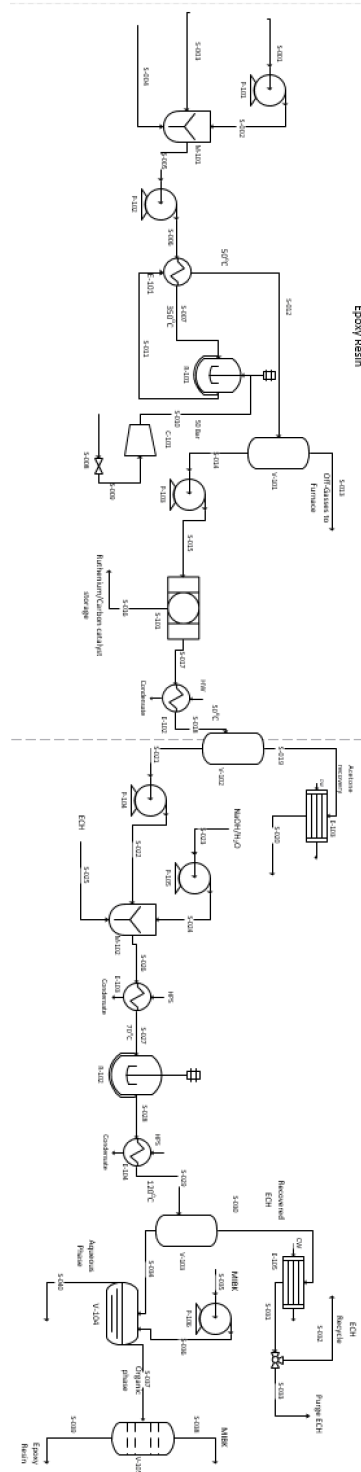
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Appendix.

Appendix A: Full PFD lignin based epoxy resin



Appendix B: Economic analysis

B.1. Lignin based Polyurethane

Polyurethane Process			
Equipment	Sizing Parameter	SP Units	Cost USD
Mixer	0,203	l/s	1184,607506
Heater	16,1235	m ² hts	29518,25579
Reactor	1,71	m ³	111420,652
Evaporator	11,82	m ²	140366,779
Condens	10,462	m ² hts	28903,50679
Pump	0,2233	l/s	8062,260283
Total cost USD			319456,0614

Solvents and Reactants				
Material	Mass kg/hr	Cost USD/kg	Cost per hour	Cost per year
THF	114,75	2,95	338,5125	2708100
MDI	398,24	3	1194,72	9557760
PEG400	526,169	2,5	1315,4225	10523380
Lignin	225,5	0,975	219,8625	1758900
Total cost				24548140

Utility Values			
Electricity	Units	Cost USD/kWhr	Cost per year USD
59,034	kW	0,129	60923,088
Water	Units	Cost USD/m3	Cost per year USD
1,084	m ³ /hr	23,62	204832,64
Total utility cost			265756

Appendix B.2. Lignin depolymerization

Epoxy Resin Depolymerization			
Equipment	Sizing Parameter	SP units	Cost USD
Mixer B1	75	kW	122170,217
Heater B2	6,81	m ²	28063,99486
Comp B3	690,751	kW	1590042,039
Reactor B4	0,96	m ³	92955,77194
Cooler B5	13,19	m ²	29193,12931
Evap B6	26,268	m ²	217593,7919
Filter B7	9,3	m ²	108563,202
Evap B8	26,268	m ²	217593,7919
Pump 1	0,398	l/s	8104,738417
Pump 2	0,396	l/s	8104,264607
Total Cost			2422384,941

Solvents and Reactants				
Material	Mass kg/hr	Cost USD/kg	Cost per hour	Cost per year
Lignin	225,5	0,975	219,8625	1758900
Ru/C	9,02	100	902	7216000
Acetone	676,5	1,062	718,443	5747544
Hydrogen	100,8	0,7955	80,1864	641491,2
Total Cost				15363935,2

Utility Values Depolymerization			
Electricity	Units	Cost USD/kWhr	Cost per year USD
434,272	kW	0,129	448168,704
Water	Units	Cost USD/m ³	Cost per year USD
2,891	m ³ /hr	23,62	546283,36
Total utility cost			994452

Appendix B.3. Lignin based epoxy resin

Epoxy Resin Production			
Equipment	Sizing Param	SP units	Cost USD
B1 Mixer	0,414	l/s	1392,216141
B2 Heater	82,15	m ²	38713,28951
B3 Reactor	1,6	m ³	108834,6693
B5 Heater	8,67	m ²	28721,13517
B6 Evaporator	26,27	m ²	217602,8899
B4 Decantor	26,27	m ²	217602,8899
B7 Evaporator	26,27	m ²	217602,8899
Pump	0,3355	l/s	8089,81203
Pump	0,2101	l/s	8045,3816
Total Cost			846605,1733

Solvents and Reactants				
Material	Mass kg/hr	Cost USD/kg	Cost per hr	Cost per yr
NaOH	27,442	0,5	13,721	109768
ECH	84,638	1,4	118,4932	947945,6
MIBK	225,05	1,2	270,06	2160480
Total Cost				3218193,6

Energy Values Epoxy process			
Electricity	Units	Cost USD/kWhr	Cost per year USD
59,982	kW	0,129	61901,424
Water	Units	Cost USD/m ³	Cost per year USD
2,71	m ³ /hr	23,62	512081,6
Total utility cost			573983