

Feasibility study of lignin valorisation at Södra Cell in  
Mörrum

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# 1. Introduction

## 1.1 Biomass and Lignin

In today's society, the vast majority of the products that are essential originate from fossil-based resources. Bio-based polymers are still used at a much lower extent. Given the knowledge of climate change, the urgent need for biochemicals is clear, and lignin seems to be a potential source for valorisation into useful bio-based chemicals.

Lignin is considered the third most abundant biopolymer and composes about 15–30 wt% of the dry biomass [1]. It has the potential as a renewable feedstock to produce biochemicals at an industrial scale, as approximately 150–200 billion tons of lignocellulosic biomass is produced annually worldwide. Biomass containing lignin is generally made of cellulose (44–50%), hemicellulose (28–31%) and the rest is lignin. Most of the biomass utilized is used in industries that primarily produce sugar, ethanol, pulp and paper, where the main sources are primarily cellulose and hemicellulose, which leads to a great surplus of lignin [2,3].

Since wood typically contains high amounts of lignin compared to biomass in general, combined the fact that the pulp and paper industry utilizes vast amounts of wood, this gives rise to about 50–70 million tons per annum of untreated lignin [3,4]. Until today, lignin has almost entirely been treated as a waste product with its main purpose of providing heat/electricity through burning. Though with its high aromatic content, lignin could be utilized for future bio-based high-value products via valorisation that potentially improves economic- and resource sustainability [5].

Historically, the amount of carbon dioxide in the atmosphere has fluctuated around 200 ppm. Within the last century, these figures have more than doubled, increasing by 2–3% every year. To stop this trend, the world must support the transition into using renewable resources and economize on these as far as possible [6]. In 2018, the industrial sector in Sweden comprised one-third of all carbon dioxide equivalents, in which the paper and pulp industry was responsible for about 6% [7]. This corresponds to approximately one thousand tons of carbon dioxide equivalents. Although, the emissions in the Swedish industry have declined linearly since 2000, it has in recent years stagnated [7].

Sweden is broadly precepted to be pioneers in greentech and environmental awareness, and it should be no exception in this case, especially when it comes to the paper and pulp industry.

## 1.2 Project Description

This project was performed in cooperation with Södra Cell Mörrum, a mill that produces both paper pulp and dissolving pulp. The mill annually generates 300,000 tonnes of paper pulp and 170,000 tonnes of dissolve. Currently, the lignin is treated as a waste product and is combusted into energy that produces electricity and district heating [8].

The aim of this project is to evaluate if it would be economically favourable to integrate a lignin-to-vanillin biorefinery into the existing site. The vanillin production should not disturb the current production at the site. An integrated process design is suggested, and a sensitivity analysis is performed on the most prominent parameters.

### 1.3 The Kraft Process

Kraft pulping is the process of removing lignin from wood by digesting wood chips in a solution of white liquor (sodium sulphide and sodium hydroxide), at an elevated temperature and pressure. The lignin, which creates a rigid three-dimensional network between the cellulose and hemicellulose fibres, is dissolved by the white liquor. This allows for the cellulose and lignin to be easily separated. The remaining mixture of lignin and white liquor is called black liquor, which is then evaporated and boiled down to remove excess water and lignin in a recovery boiler. This process also produces a large amount of steam, which is typically used to power and heat the paper mill. The remaining green liquor (spent cooking chemicals) is then restored to its original composition when it is added to lime in a kiln [9].

Two major advantages of the Kraft process are the production of heat and the easily recoverable cooking chemicals. However, the Kraft process produces considerable amounts of pollutants; particularly sodium and calcium salts from the lime kiln. Other odorous and potentially harmful compounds, such as hydrogen sulphide, methyl mercaptan and dimethyl disulphide, are produced by the Kraft process.

### 1.4 Vanillin market and history

Vanilla has been an enjoyable flavor in food since it was first brought to Europe in the 1500s. In the middle of the 1800s vanillin was identified as the main flavor component and less than 20 years after that, the first synthetic vanillin was produced. Until the 1990s the majority of all synthetic vanillin was produced from lignin but most plants closed when cheaper vanillin could be produced from petroleum without the highly caustic solvent.

Today, Borregaard in Norway is the only producer left of synthetic vanillin from lignin and holds about 15% of the global market. Vanillin from the vanilla bean is very rare and expensive, and less than 1% of all vanillin originates from the vanilla bean. The rest of the produced vanillin originates from petroleum [10].

The worldwide demand of vanillin is about 20,000 tonnes per year [10]. Vanillin is today mainly used as flavour or aroma in the food & beverage and fragrance industries. But it is also used to some extent in the pharmaceutical industry. A report made in 2017 predicted that the vanillin market would have a compound annual growth rate (CAGR) of 7.66% and show a growth in all the three largest areas [11]. Numerous research efforts are currently going on to replace fossil-based chemicals and fuels with bio-based alternatives. The fact that vanillin is a stable aromatic molecule makes it a possible candidate to replace bisphenol A in the chemical industry [10]. Then the world demand would increase to 7.2 million tonnes [12]. If vanillin was part of the base chemical industry, the CAGR value would be much higher than 6.2%.

## 2 Literature Study: Lignin Valorisation

### 2.1 Technical Lignin

The irregular amorphous polymer of lignin consists mainly of phenylpropanoid monomers which creates a three-dimensional network. These monomers are syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H). Although the precise structure of lignin is unknown due to its high complexity, one has found the most abundant bonds within the structure. These bonds consist approximately of one-third C-C linkages and two-thirds ether bonds. The stronger C-C bonds being  $\beta$ -1,  $\beta$ -5 and  $\beta$ - $\beta$  and the weaker ether bonds  $\beta$ -O-4,  $\alpha$ -O-4 and 4-O-5. Kraft lignin contains a significant amount of sulphur as it has impurities where it bonds with sulphur species. This can hinder the valorisation process due to sulphur's poisonous characteristics [3].

Kraft lignin differs from native lignin as the Kraft process changes the structure of the lignin. Lignin in this form is called technical lignin [3], and this contains some sulphur and sodium that cleaves the interlinkages in the lignin and forming smaller lignin fragments that are also more water-soluble, resulting in the dissolving into the black liquor [3].

Lignosulfonates has for several years, been the market leader when it comes to technical lignin feedstocks. Since the production of Kraft lignin has increased by approximately 150% from 2014 to 2018 it becomes an interesting alternative for further valorisation as the gap to lignosulfonates is closing [14]. In addition, Kraft lignin processes are worldwide, and up to 90% of the extracted lignin is derived from a Kraft lignin process, which makes it a viable raw material for lignin production ahead [15].

### 2.2 Valorisation of Lignin

Since lignin is an abundant resource, it has attracted attention in recent years for use as a precursor of more valuable products. Valorisation of lignin involves a depolymerisation and the compounds produced and their amounts depends on depolymerisation method. However, the focus of this report will be on vanillin, acetovanillone and vanillic acid which are common products from the oxidative depolymerisation of softwood lignin [1]. Of these products, vanillin is especially a desired product as it is used widely in the food industry. Further products that could be formed are other aromatics and carboxylic acids [16]. The purity of vanillin for technical use should be at least 97%, and for food-grade, the purity of vanillin is required to be at least 99.8%.

### 2.3 Oxidative Depolymerisation

The depolymerisation can be done in many different ways, and these methods can be categorised into mechanical, chemical, physio-chemical and biological. However, depending on the method, the product mixture differs. It has been found that oxidative depolymerisation together with a Cu/Mn catalyst achieved promising results regarding depolymerisation of lignin into high-value products such as vanillin, vanillic acid and acetovanillone. The oxidative depolymerisation method has the ability to produce highly functionalized chemicals at moderate temperature and pressure [16].

Abdelaziz et al. [1] found that by using oxidative depolymerisation, other valuable products from the ones already mentioned are formed such as phenolic acids, other phenolic aldehydes

and carboxylic acids. Furthermore, oxidative depolymerisation was found to be an energy-efficient method, with an operation temperature near 160 °C in comparison to other lignin depolymerisation approaches, such as hydrothermal depolymerisation, pyrolysis, etc. [1].

## 2.4 Separation of valorised products

The oxidative depolymerised product mixture contains a broad distribution of molecular weight (MW). Depending on the treatment conditions, for example, pH, temperature and pressure, different MW distributions (MWD) are expected. A typical softwood Kraft lignin was depolymerised with oxygen present under alkaline conditions, and the MWD was compared with untreated lignin [1]. The results indicated that the polymers reduce from larger than 10 kDa down to smaller than 5 kDa at optimal conditions, whilst some monomers form as described previously in section 2.3 [1].

Thereafter, to obtain the valuable products, the larger parts of the unreacted lignin has to be separated at first not to interrupt the downstream treatment. This could be made possible by acidifying the solution until the large fragments precipitate or via ultrafiltration. The acidified solution could then be processed in many ways. One of them is by extracting the phenolics with an organic solvent to recover the phenolics in an organic phase for further separation. Another method could be to use adsorption for isolating the phenolics from the acidified reaction solution [10].

## 2.5 Liquid-liquid extraction

For current industrial processes producing synthetic vanillin, the separation is often made possible due to liquid-liquid extraction. Firstly, the reaction mixture has to be acidified as explained previously and then follows contacting the stream with a solvent stream. This solvent has to be chosen carefully so that it extracts the products to a high degree without contaminating the end product. A suitable solvent for this application could be ethyl acetate due to its solubility of  $1.23 \times 10^{-1}$  mole vanillin/mole water [17] In addition, ethyl acetate is classified as generally regarded as safe (GRAS), which makes it safe for producing vanillin added in foods [18].

## 2.6 Adsorption

Researchers from the Laboratory of Separation and Reaction Engineering at the University of Porto in Portugal have explored the possibilities of separating depolymerised kraft lignin under alkaline conditions via first ultrafiltration and afterwards adsorption onto an SP700 resin, followed by different desorption methods [19].

### 2.6.1 Adsorption with two steps desorption

A separation of the key products vanillin (V), acetovanillone (VO) and vanillic acid (VA) from the reaction mixture was made, which was able to separate each compound to three distinct phases. The phases grouped the molecules according to the structures, ketones, aldehydes and acids. Firstly, the reaction mixture was ultra-filtered through a membrane with a molecular weight cut-off (MWCO) at 5 kDa at trans-membrane pressure of 20 bar and 25 °C. Sulphuric acid was then added to the permeate to view the effect of pH in the adsorption step [19].

The acid-treated permeate was then sent to the adsorption column, and the feeding took place until the equilibrium of the adsorbed compounds was reached. Thereafter the desorption was started, and two eluents were used for the same amount of time. The first was deionized water and second ethanol. The results at pH 10 show that approximately 95% and 30% of the vanillin and acetovanillone respectively that was fed to the column, was desorbed in the water phase. The vanillic acid adsorbs minimally to the packed material and exits with the feed [19].

#### 2.6.2 Adsorption with water as eluent

In a later study, Gomes and Rodrigues explored the possibilities of adsorption of V, VA and VO from a depolymerized lignin under alkaline conditions using only water for desorption. The procedure followed the same principle setup, but the membrane filtration focused on even smaller fragments. This filtration was performed by two membranes with MWCO at 1,000 and 600–800 Da, respectively. The first filtration operated at 8 bar and the second at 30 bar at 25 °C. The permeate was then fed to the adsorption column, and the cycles of adsorption/desorption were done. In the first outlet stream (outlet of the fed reaction mixture), the vanillic acid is enriched as it barely adsorbs in the column. In the second outlet stream that uses water as eluent, vanillin and acetovanillone is present and up to 70.7% and 84.5% of the respective molecules is recovered from what was fed to the column. [20]

The main advantage of using the latter adsorption with deionized water as eluent compared to the traditional separation methods with acidifying and organic solvents is the avoided costs of both these chemicals (including their recycle loops and losses). Also, since no acid is added to the reactor products, the retentate could be returned to the cooking process without disturbing the chemical balance of the mill. Alternatively, it could be recycled back to the reactor for further depolymerisation.



### 3 Process Design

The majority of the unit operations are designed using simple mass-balance calculations by hand combined with a reactor modelled in Aspen Plus® commercial software.

#### 3.1 General Assumptions

The work with process design followed the onion model, where the process is built from the reactor, and from there, the rest of the process was developed with separation processes and utilities. The choice and conditions for the reactor and its stoichiometry are based on experimental data (unpublished raw data). For this model, only the products of vanillin, vanillic acid and acetovanillone were assumed and were accounted for in the separation. It was assumed that off-gases were instantly removed in the reactor, which means that all the possible by-products were not accounted for. The design of the separation was inspired by two recently published articles on the purification of the product stream resulting from lignin oxidation to valuable monomers [15,20]

More information and data about the different unit operations will be presented in the following sections, and the resulting process is shown in Figure 1. Unit operations, such as the reactor, the pumps, and the heat exchangers were modelled using Aspen Plus, while the rest were set as separators due to simulation difficulties.

A general assumption that is valid for the whole process is that the solution has a density similar to water,  $1000 \text{ kg/m}^3$  with no thermodynamic effects as mixing-enthalpies as this is an early-stage feasibility study.

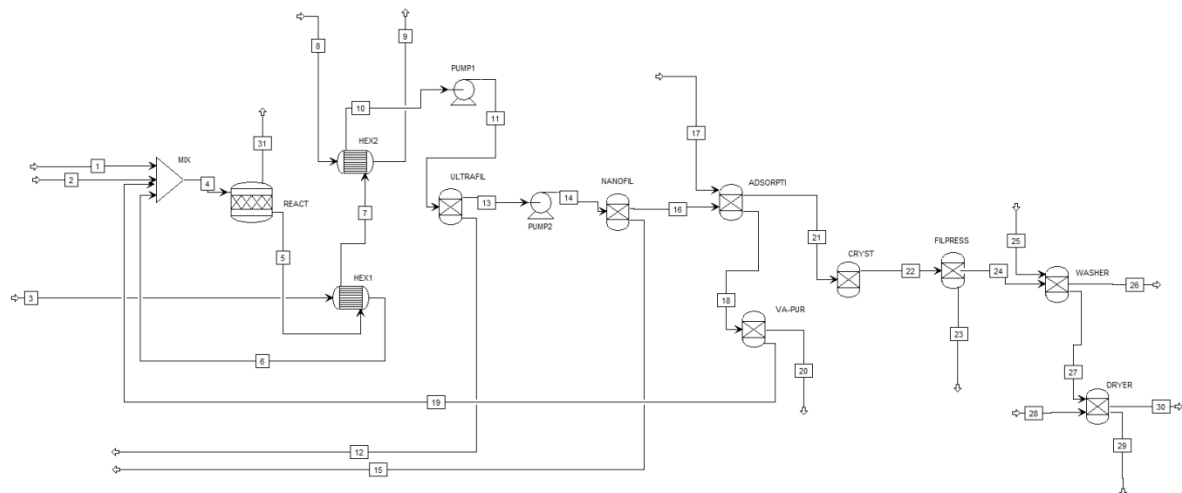


Figure 1: The modelled process for valorising lignin into the three monomeric products.

Another important assumption that has been made is the type of catalyst involved in this process. The type of catalyst was a homogenous bimetallic catalyst, which is based on unpublished work. It is important to use appropriate material for all the units to avoid corrosion of the units. The flow into the reactor is a highly alkaline NaOH-solution, and after the adsorption, the flow can be assumed to be water. From the corrosion guide in chemical engineering [21], stainless steel was found as an appropriate material to be used in all units.

## 3.2 Unit Operations

The more detailed design of the specific process units is described in the following section, with operating conditions and dimensions.

### 3.2.1 Reactor

First off is the reactor, which was assumed a continuous-stirred tank reactor (CSTR). To the reactor, streams of weak black liquor, pure oxygen at 5 bar, and the catalyst were fed. The volume of the reactor was assumed to be 46 m<sup>3</sup>. More detailed conditions are used from unpublished work.

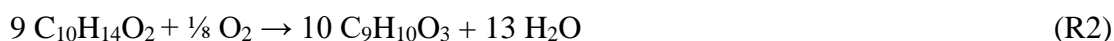
The yields based on wt% of lignin from the reactor are assumed to be as described in Table 1.

*Table 1: The yields of the valorized products in the reactor*

<b>Product</b>	<b>Yield</b>
Vanillin (V)	0.035
Vanillic acid (VA)	0.028
Acetovanillone (VO)	0.005

The reactor was simulated using Aspen Plus v10. Lignin is, as described earlier, a very complex compound that is difficult to account for its modelling. Therefore, for this report, the lignin was assumed to be 2-methoxy-4-propylphenol (C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>, MW= 166 g/mol) [22].

The valorisation of lignin was simulated by these three reactions that converted the assumed model compound into the desired products via oxidation, where the first reaction describes vanillin, the second acetovanillone and the third vanillic acid:



### 3.2.2 Membrane Filtration

The membrane filtration was performed by ultra- and nano-filtration steps in series, which both operated at 25 °C. Key assumptions made were:

- Even split of concentration of products in permeate and retentate
- 95% of lignin remains in the retentate
- 10% of the feed leaves as retentate (based on water content).

The assumption about even split of concentration of products was based on the fact that all three substances have a tendency to be deprotonated at such high pH ~13 [20]. This results in the substances being ionized and are therefore very likely to follow the water.

The chosen type of membrane was spiral wound membranes were used as they are both cost-effective and can handle fouling relatively well [21]. In the first filtration, an ultra-filter with a MWCO of 1,000 Da running at 8 bar was used. And in the second, a nano-filter with filtration of 700 Da running at 30 bar was used. The retentates were returned to the mill with the assumption that these lignin fragments in the stream were not possible to further depolymerised in the reactor. The permeate was then sent to the first adsorption column for further separation.

After investigation together with Synder<sup>®</sup> Filtration [23], a feasible setup of the filters was produced. Using their XT-2B-8038 element for the 1,000 Dalton filtration, 12 elements would be needed. Each element had a surface area of 37 m<sup>2</sup>, i.e. 444 m<sup>2</sup> in total. For the 700 Dalton filtration, the NFG-2B-8038 element was used, and 16 elements were needed. Each with 34 m<sup>2</sup> surface area per piece or 547 m<sup>2</sup> in total.

### 3.2.3 Adsorption Column 1

After the larger lignin-constituents were removed from the product mixture, the separation of the three products could begin. This was made via adsorption using a non-polar resin called SP700, which is made of polystyrene divinylbenzene (PS-DVB). An alternative to this adsorption could have been liquid-liquid extraction. However, one downside with introducing a solvent where the valuable substances would partition to is the fact that some solvent will dissolve into the reaction mixture. This implies that sending the reaction mixture back to the mill may disturb the chemical balance of the Kraft process, which is not favourable. Also, there could be a greater loss of catalyst compared to adsorption if the solvent allows for the transfer of the catalyst.

The column was designed using Karlsson's adsorption guide [24]. This handbook bases its design of adsorption columns on relatively simple correlations regarding the behaviour of fixed bed adsorptions, which was used for this column.

Firstly, data for the adsorption process has to be obtained. Mota et al. [25] have studied the adsorption of vanillin onto the SP700 resin both experimentally and theoretical by simulating mathematically a fixed bed. What they found was that vanillin adsorption was experimentally best described by the Freundlich adsorption model, which had the following expression:

$$q_e = KC_e^{1/n} \quad (\text{Eq 1})$$

where  $q_e$  is the absorbed amount of vanillin onto the resin at equilibrium (g vanillin/g dry resin) and  $K$  is a constant of relative capacity of absorbent and  $C_e$  is the concentration at equilibrium and  $n$  is the Freundlich exponent. For their experiment at 298 K a  $K$  value of 0.335 g vanillin  $g^{-1}$  dry resin  $(L/g)^{1/n}$  was obtained together with a Freundlich exponent of 2.7 [25]. In addition, it was found that the average particle diameter of the resin was 450  $\mu\text{m}$ , and used for the simulation a dispersion coefficient of  $1.04 \times 10^{-4} \text{ m}^2/\text{min}$  and an effective pore diffusion coefficient of  $2.62 \times 10^{-8} \text{ m}^2/\text{min}$  [25]. In the study by Gomes and Rodrigues [20], the same resin was used on a real solution of oxidized lignin products, and they reported a column porosity of 0.37. All of these parameters were then used in the design of the adsorption column.

After the collection of the parameters, the geometries were identified based on assumed velocity and column length, and the final values are given in Table 2.

Thereafter, the mass transfer effects due to dispersion, the outer mass transport and pore diffusion were estimated. The mass transfer, which affects the separation the most is determined as the limiting step, but in this case, none had such a big influence.

One thing worth noting is that Karlsson [25] points out that there is a higher limitation of the flowrate at approximately 0.08  $\text{m}^3/\text{s}$ , which the process exceeds when taking regeneration time into account. Due to this fact, two identical adsorption columns were designed to work in parallel with an approximation of that the regeneration time is equal to the breakthrough time.

When it comes to the regeneration of the column, deionized water was used as described in Gomes and Rodrigues [20]. This implies no need for implementing a solvent to the process. The total flow of the water was set so that the outlet concentration of vanillin is 4.7 g/L, which makes this solution possible for crystallization at approximately 18.7  $^{\circ}\text{C}$  [26].

The pressure drop over the column will be around 20 kPa/m according to the datasheet provided by Mitsubitshi [27] which adds up to a total pressure drop of 60 kPa.

Table 2: Column specifications used for adsorption

L - Length	3.0 m
------------	-------

D - Diameter	3.0 m
Q <sub>F</sub> - Flow rate feed	0.034 m <sup>3</sup> /s
Q <sub>e</sub> - Flow rate eluent	9.3×10 <sup>-3</sup> m <sup>3</sup> /s
t <sub>b</sub> - Breakthrough time	41 h
t <sub>c</sub> - Cycle time	82 h
m - Mass of adsorbent	14.2 tonnes

### 3.2.4 Crystallizer

From the adsorption, the saturated vanillin stream enters the crystallizer, which operates at 18.7 °C. This temperature was determined by using a polynomial equation for the solubility of vanillin in water [26]. The losses in the crystallizer and the following filter press were assumed to follow the losses described in Khwanjaisakun [15].

To be able to accurately calculate the size and cost of such a crystallizer the crystal growth rate for vanillin is needed. The vanillin crystallization rate constants were not found, and therefore it was assumed that the rate constant K<sub>R</sub> for vanillin was in the same range as other compounds described in the book Crystallization by Mullin [28]. The crystal growth rate G was calculated using the following equation [28].

$$G = \frac{30}{\alpha \rho_c K_R L_M^4} \quad (\text{Eq 2})$$

It was assumed that both the number nucleation rate and the crystal growth rate was first order. The volume shape factor was not found in any research for vanillin and was assumed to be 0.8, a typical value for other crystals. The density for vanillin crystals c is 1,060 kg/m<sup>3</sup>, and the median size of the crystals was assumed to be 300 μm to minimize the losses in the filter in the next step. With a K<sub>R</sub>-value of 5×10<sup>18</sup>, the crystal growth rate was 9×10<sup>-7</sup> m/s [28].

The crystallizer will be run continuously, but price estimations for crystallizers were only found for batch-wise crystallization. Therefore, it was assumed that the cost for a batch crystallizer was equal to the cost of a batch crystallizer with the same capacity. Using the growth rate specified earlier and a method specified by Mullin [28], the size of the batch crystallizer was calculated as 34 m<sup>3</sup>.

### 3.2.5 Filter Press

The formed vanillin crystals were assumed to have a median size of 500 μm. To separate them from the liquid, a filter press was used. A fabric filter would be able to separate small particles <20 μm and therefore be sufficient to separate the crystals [29]. The liquid where the solid vanillin has been extracted from still had high amounts of NaOH and should have had to be

treated before it could be extracted. The loss in the filter press was 9.7% according Khwanjaisakun et al. [15].

### 3.2.6 Washing step

The next step in purifying the vanillin stream was washing to remove impurities. This was done by adding water under mild conditions to mostly dissolve the remaining impurities with as little loss as possible of vanillin. When it comes assumptions of products, 10 wt% of acetovanillone and vanillic acid is assumed to be dissolved with 0.04 wt% of the solid vanillin [15].

### 3.2.7 Dryer

After most of the impurities were washed away, some water had to be evaporated from the vanillin crystals in order to obtain food graded vanillin at 99.8%. This was done in a dryer that uses air at approximately 40 °C and atmospheric pressure to reduce the water content of the final product, food graded vanillin [15].

### 3.2.8 Adsorption Column 2

The second adsorption column was added to separate vanillic acid from the rest of the substances, including the catalyst. This makes it possible to recycle the catalyst and water to the reactor while also purifying and crystallizing the VA. However, there were difficulties in designing the separation of vanillic acid as the information about it is limited and finding an adsorbent to use was a difficult task as the only research done was on the same SP700 resin as earlier used [27]. The plan was to perform a similar adsorption process as previously done for vanillin. However, problems might occur, such as VA not adsorbing, and the solubility of VA was not found.

### 3.2.9 General Losses throughout the Process

The major losses of chemicals that are supposed to be recycled in this process will be the sodium hydroxide, water and the catalyst. If one were to look into the membrane filtration, it is assumed that 10% of the ingoing water together with the solutes are being lost which are directed to the mill. An assumption we are making is that the sodium hydroxide that is directed to the mill will be returned to the reactor.

Losses also exists in the adsorption columns in terms of NaOH, about 3% per adsorption column. This is based on Gomes and Rodrigues [20] where a solid content analysis of the vanillin rich solution and the permeate solution from the nano-filtration was made.

When comparing the permeate, an inorganic solid content of 78 g/L was identified compared to around 4 g/L for the vanillin rich solution. Since the reactor was fed with 80 g/L of NaOH in their experiment, it is reasonable to assume that all of the inorganic solid content is NaOH. This is what underlies the assumptions of 3% loss in the adsorption column.

### 3.2.10 Integration into the existing pulp mill

The feedstock for our reactor is as previously described as weak black liquor, so there would be an outtake after the cooker. Then the retentate stream will be redirected to the recovery boiler, which is highly concentrated.

## 3.3 Energy Analysis

The energy analysis was performed in Aspen, by simulating the process streams according to Appendix A and enabling the program to calculate the energy usage. Thereafter heat exchangers were added to minimise the energy consumption of the process. Cooling water was available from Södra Cell at 10–20 °C. Södra Cell also had steam available at 10 bar and 200 °C.

### 3.3.1 Heat Exchanger

The warm stream after the reactor and cooling water at 15 °C were utilized by the addition of two heat exchangers which were introduced in Aspen Plus. The purpose was to heat up the solution before entering the reactor using the stream after the reactor, which in turn cools the second stream. A second heat exchanger was added to further cool the product stream entering the membrane filter down to 25 °C using cooling water.

The design choices for the heat exchangers were based on a fixed shell and U-tube heat-exchanger. The overall heat transfer coefficient was approximated and assumed as 1 kW/m<sup>2</sup>/C, which was within the range of typical values of such a heat exchanger [30]. Through Aspen, the first heat exchanger was calculated to require an exchanger area of 795 m<sup>2</sup> and the second one required an exchanger area of 1,117 m<sup>2</sup>. Other units that had an energy requirement were neglected due to the considerably small amounts of energy usage.

## 4 Economics

### 4.1 General Assumptions

One US dollar was assumed to be equal to 9.9 SEK, based on the average exchange course during April 2020. When using the CE plant cost index, an average for 2019 was used, which equals a value of 607.5 [31].

#### 4.1.1 Product Prices

The income for the investments comes from selling the products. In this project, the main assumption has been that only vanillin, acetovanillone and vanillic acid was formed. Vanillin has had the largest mass of the three, and therefore the separation process mainly focused on purifying vanillin.

Prices for the three products can be found in Table 3. These are estimated mean prices from different producers, mainly on the website Alibaba.

*Table 3: The assumed sale prices and price ranges for the three main products.*

Compound	Assumed price (SEK/kg)	Price range (SEK/kg)
Vanillin	150	50-300
Acetovanillone	2000	1000-3500
Vanillic acid	300	100-1000

The production rate of vanillin was 128.8 kg/h, according to the mass balances in Appendix A, It was assumed that the process could operate at around 8000 hours per year. In the current process, either acetovanillone or vanillic acid are purified into products. The production and the possible annual income from product sale is described in Table 4. Those numbers assume that all produced products could be sold to the prices described in Table 3: The assumed sale prices and price ranges for the three main products. Table 3.



Table 4: The production and the possible annual value of the respective product

Compound	Production (kg/h)	Annual product value (MSEK)
Vanillin	128.8	154.5
Acetovanillone	18.4	294.6
Vanillic acid	103.1	247.5

The possible value for both acetovanillone and vanillic acid are very large, but the market situation is more unclear than the situation for vanillin. Also, there is no current method available for the separation of those components from the reactor mixture in this process. But if a good separation process is constructed and the market is analysed for either acetovanillone or vanillic acid there is a good opportunity to improve the overall investment.

#### 4.1.2 Material and Utility Costs

The main utilities that will be involved in the operational costs are water, steam and electricity. The assumed prices are summarized in Table 5 below:

Table 5: Feedstock and utility costs involved in the operation.

Resource	Price	Unit	Source
Water	0.5	SEK/m <sup>3</sup>	[32]
Electricity	0.5	SEK/kWh	[33]
Oxygen	900	SEK/ton	[34]
Steam	60	SEK/ton	[34]
Sodium Hydroxide	3000	SEK/ton	[35]
Lignin	5000	SEK/ton	[36]
Catalyst (Copper/Vanadium)	400	SEK/kg	[37]

#### 4.1.3 Grass Roots Cost Estimation

When trying to estimate the different costs, both operational and investment costs, some general assumptions have been made, and some prices have been fixed. These will be presented in the following section.

In order to estimate the total investment cost, Ulrich's method will be used to obtain the grass-root plant cost. When it comes to the estimation for the investment cost, the bare module cost must be estimated and is based on some assumptions and are represented in Table 6 [37].

Table 6: Assumptions related to the calculation of the bare module cost of equipment.

Type	Percentage (%)	Based on
Auxiliaries	100	Equipment cost
Installation	53	Equipment cost
Ground improvements	15	Equipment cost
Freight and insurance	4	Equipment cost
Installation overhead	70	Installation cost
Engineering	16	Direct cost

To obtain the gross-root cost, the sum of the bare module costs was multiplied by two factors that tries to capture the costs of fees and contingency as well as auxiliary facilities.

## 4.2 Capital Cost Estimation

The capital cost of the different unit processes is described below. The total bare module cost was 89 million SEK. Adding a fee and contingency factor of 1.15 and auxiliary facilities of 1.25, the gross-root cost comes to 129 million SEK.

### 4.2.1 Reactor

A reactor with a diameter of 4 meters and a height of 4 meters was required, equating to a total volume of 46.4 m<sup>3</sup>. Using EconExpert [38], a jacketed reactor, operating at 5 bars, would imply a bare module cost of 4 MSEK.

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### 4.2.2 Membrane filtration

The membrane filters mentioned in section 3.2.3 were sourced through Sydner® Filtration. These were quoted at an estimated about 12,000 SEK per piece, for a total of 336,000 SEK. These filters are assumed to be changed every quarter, which leads to an annual cost of 1,344,000 SEK. This change of filters implies an additional cost factor of 40%, ending up at 1,863,000 SEK or 1.86 MSEK

EconExpert [38] was used to calculate the bare module cost of the setup itself, including pumps. Using the nano-filtration model, the 1000 Dalton setup has a bare module cost of 8.88 MSEK, and the 700 setup received a cost of 10.3 MSEK.

#### 4.2.3 Adsorption column 1

In order to estimate the total investment cost of the adsorption column, the cost of packed material and the tower itself had to be estimated. When it comes to the packed material, the total mass was multiplied by the price (per mass) to give the packing cost. The price for the housing of the column was found using EconExpert [38] by selecting a stainless steel, vertically oriented process vessel without packed material with the dimensions found in Table 2 together with a pressure factor of 1. This gave a bare module cost of 5.71 MSEK for the housing per column. The packed material had a purchase cost of 3.27 MSEK totally for both columns. Together, the first adsorption column resulted in a bare module cost of 16.6 MSEK.

#### 4.2.4. Crystallizer

The size of the crystallizer was estimated to 34 m<sup>3</sup>. The purchase cost of the crystallizer was estimated using the Matches' Equipment Cost Estimates [39]. With input of volume and material, the purchase cost of the crystallizer was estimated to 5.9 MSEK at 2014 years value. The average CE Plant Cost Index value for 2014 was 576.1 and therefore the bare module cost in today's value was 21.6 MSEK

The assumptions made above regarding the crystallizer seems to be quite accurate because the purchase cost of a slightly larger crystallizer used to crystallize sophorolipids in a biorefinery is about 8 MSEK. The flow there is about 175 kg/h of crystallized material which is about 15% larger than the flow in this process [40].

#### 4.2.5 Filter press

The mass flow through the filter was according to the Appendix A about 34 m<sup>3</sup>/h, containing 130 kg dry solids. The Benenv MDS-413 is an appropriate filter press to use. It is a filter press designed for treatment of wastewater, but it should be applicable for this purpose as well. The capacity, according to the company home page, is a flow of 18–60 m<sup>3</sup>/h containing 120–180 kg DS/h [41]. The purchase cost of this equipment is 100,000–900,000 SEK [42] and it is assumed to cost 500,000 SEK. To get the bare module cost of the filter press the purchase price is multiplied with the factors from Table 6 gave a bare module cost of 1.8 MSEK.

#### 4.2.6 Washer

A corkscrew-style, sand washer was selected [43], with an assumed purchase cost of approximately 49,500 SEK. By applying the material factor of 2 (based on the requirement of stainless steel), the purchase cost of the washer is 99,000 SEK. Including 40% for installation, the bare module cost is 138,600 SEK.

#### 4.2.7 Dryer

The purchase cost for this unit was estimated using the following equation:

$$C = (M\&S \text{ cost index}) \left( 30 + 36.74 \times \frac{W}{17.77+T} \right) \quad (\text{Eq 3})$$

where M&S cost index is the current Marshall and Swift Cost Index,  $W$  is the evaporation capacity in kg/h and  $T$  is the temperature of the inlet air in °C [44]. This equation gives a rough estimate for the cost for steel dryers with auxiliaries. Since the M&S cost index came to an end in 2012 it was estimated with CE plant index instead. Using the assumption that an CE index of 400 corresponds to an M&S index of 1100 the cost could be calculated [38]. In order to estimate the price of a stainless-steel dryer from carbon steel, a material factor of 2 was used. This resulted in a bare module cost of 1.8 MSEK.

#### 4.2.8 Adsorption 2

There is not much research done on the separation of vanillic acid with an adsorption column. To get an estimation of the cost of this separation step, it was estimated that the cost per kilogram solid that gets adsorbed will be the same as the first adsorption column. The calculations are presented in Table 7. Also, it was assumed that only the vanillic acid was adsorbed in the second column.

Table 7: Cost comparison between the first and second adsorption column.

Item	Adsorption 1	Adsorption 2
Adsorbed mass	182.6 kg/h	147.5 kg/h
Total cost per kilo adsorbed material	90,700 SEK	90,700 SEK
Total bare module cost of column	16.56 MSEK	13.37 MSEK

#### 4.2.9 Heat Exchangers and Steam Consumption

To lower the heat requirement of the process, heat integration was performed with two heat exchangers. It was assumed that they were shell and tube exchangers with the areas specified in section 3.3.1. EconExpert was used to estimate the bare module cost for the exchangers. The bare module cost for the first exchanger was 4.42 MSEK and 6.7 MSEK for the second heat exchanger [38].

### 4.3 Operational Costs

The operational costs involved in the valorisation of lignin are typical for most chemical processes. These costs can be broken down into fixed capital expenses (storage and spare parts), manufacturing expenses (materials, labour, utilities, and licencing) and indirect expenses (overheads, administration, sales and R&D). The operational costs in terms of electricity will most likely be negligible and the majority will be maintenance and repair.

These costs can vary greatly and are difficult to estimate at a feasibility stage, so several assumptions and 'rules of thumb' were incorporated into our model. To support our process, the "Rules of Thumb for Chemical Engineers" [33] was relied upon.

When calculating the net present value (NPV) of this investment, several economic-related parameters have been assumed. Firstly, it is expected that the company can borrow approximately 80% of the total investment costs, at a rate of approximately 2.4%. The remaining 20% comes from company capital, at an expected return of 11%. This gives a weighted discount rate of 4.12%. A salvage value of 0 has also been assumed.

#### 4.3.1 Fixed Capital Expenses

Storage costs can be split into storage for products and feedstock. Since our feedstock (lignin) comes directly from the primary pulping process, we assumed that storage for this would not be required. However, for products, it was assumed that the maximum recommended time in storage, 60 days, was likely. This was to aim towards more of a 'worst case scenario'. The associated cost of storing products can be calculated as follows:

$$\text{Annual Cost} = \frac{Q \times f_a \times P \times D}{365} \quad (\text{Eq 4})$$

Where Q is the annual production in tons,  $f_a$  is the annuity factor (related to the estimated plant life and interest rate), P is the cost/ton of product (assumed at 150,000 SEK/tonne), and D is the number of days in storage. The annuity factor is determined as:

$$f_a = \frac{X}{(1 - (1 + X)^{-N})} \quad (\text{Eq 5})$$

Where N is the economical plant life (assumed 10 years) and X is the discount rate (set at 4.12%). This results in an annuity factor of 0.124. Therefore, the total annual storage cost of products is:

$$\text{Annual cost} \left( \frac{\text{SEK}}{\text{yr}} \right) = \frac{1030 \times 0.124 \times 150\,000 \times 60}{365} = 3,149,260 \text{ SEK/year}$$

Spare parts can be estimated as 10–20% of maintenance and repair costs. Considering the membrane filters require regular replacement, 20% was selected. By applying the annuity factor of 0.13, this resulted in a total cost of 140,000 SEK/year.

#### 4.3.2 Direct Costs

In terms of feedstock supply costs, only that of water and sodium hydroxide streams was considered. The cost of lignin was neglected, as it is a side-product of the existing Kraft process at the plant. Alternatively, the revenue acquired for burning lignin could have been used here (i.e. as a lost opportunity cost).

The catalyst used in this process is copper-vanadium based. Assumed losses of this material were 10%/hour, which is based on the amount of retentate set back to the mill. At a proportion of 10% wt/wt catalyst-to-lignin, this equates to a yearly cost of approximately 206.8 MSEK/yr.

Total water-usage and cost was based upon the dimensions of our reactor (the main vessel requiring water). From this, a required feed volume of approximately 201 m<sup>3</sup> was determined. It was assumed that water was lost at 10%/hour, at a rate of 0.5 SEK/m<sup>3</sup> (32). By incorporating our estimated losses, it was estimated that the supply of water would cost approximately 80,400 SEK/year.

Sodium hydroxide is an important feed material in this process. Referring to section 3.2.3, a loss of 5.9%/hour of the original feedstock was estimated. At 2 M concentration, 0.95 tonnes of NaOH should be added every hour (based on an initial feedstock requirement of 16.1 tonnes). At approximately 3000 SEK/tonne, this equates to an operating cost of 22.8 MSEK/year.

To estimate electricity costs, total usage must first be established. A short summary of the electricity requirements for the most effluent equipment pieces is summarised below in Table 8.

Table 8: Electricity consumption for the process.

Equipment	Power Requirements (kW)
Reactor	75
Pumps (x2)	215
Washer	2
Dryer	4
	TOTAL
	296 kW

Hall [33] states that "the average cost of electricity is \$0.05/kWh (0.5 SEK/kWh)". Based on 8000 operating hours a year and an energy usage of 296 kW from valorisation, the total electricity cost (in SEK) was estimated to be 1.18 MSEK/year.

When considering electricity costs, it is important to note that lignin is being removed from power generation, in order to supply the valorisation process. Also, electricity needs for the entire plant are now increasing, due to the addition of the new process. Therefore, when implementing this new process, there may need to be a balance between burning lignin and using it to produce high-value products. Pulp mills could increase production or source alternative electricity means to fuel operations.

The addition of heat exchangers considerably lowered the amount of energy needed for heating, the reactor still required 10.4 kW to heat up the ingoing streams. Since there is steam available at 10 bar, this will be used for heating the inlet to the reactor.

The steam usage will be calculated by a simple energy balance as follows:

$$Q = m_{steam} \Delta H_{vap}(10 \text{ bar}) \quad (\text{Eq 6})$$

Where Q is the energy needed for heating the inlet,  $\Delta H_{vap}(10 \text{ bar})$  is the vaporisation enthalpy at 10 bar which is 2,777 kJ/kg and  $m_{steam}$  is the mass flow of steam.

The steam consumption was 3.74 kg/s or 107,800 ton/year. Using a steam price of 60 SEK/ton [34] this equals 6.47 MSEK/year.

Typically, steam is used to provide district heating and additional electricity for the plant and nearby area, which produces some savings for the plant. Like with electricity costs, these lost savings could be recovered by increasing pulp production or increasing the valorisation of lignin when there is a large surplus of steam, or electricity prices are low.

Oxygen was considered at a rate of 900 SEK/ton. Based on a yearly consumption of 20,849 tonnes per year, this equates to a cost of 18.76 MSEK/year.

Another important cost to consider is that of maintenance and repair. According Hall [33], maintenance and repair can be estimated at 2-10% of the grass roots capital cost. As this process involved membrane filtration that regularly requires replacement membranes and maintenance, 5% was selected. This resulted in a cost of approximately 5.37 MSEK/year (based on a grass roots cost of 107.5 MSEK).

The operator and supervisor requirements and costs were calculated using Ulrich [21]. One operator per shift is required to run the valorisation process. Assuming five shifts per week, at a 30,000 SEK/month wage, the total operator cost per year is 1.8 MSEK/year. Supervision costs can be taken as between 10 to 30% of operating labour [21]. As this process is being added on to an existing plant, it is likely that this cost will be on the lower end of the spectrum. Therefore, 10% was selected, at a cost of 180,000 SEK/year. Factoring in another 180,000 SEK/year for laboratory costs, the total direct labour costs is 2.16 MSEK/year.

#### 4.3.2 Indirect Costs

Staff overheads include 70% for shift personnel, which totals to 1.51 MSEK/year.

Administration costs are 25% of staff overhead, totalling 378,000 SEK/year.

0–10% for distribution and sales, 5% on top of total revenue selected as this is quite a large quantity of the vanillin market. Total revenue is estimate at 155 MSEK/year, producing a distribution and sales cost of approximately 7.73 MSEK/year.

The breakup of operational costs is summarised below, in Table 9.

Table 9: A summary of relevant operational costs

<b>Category</b>	<b>Cost (SEK/year)</b>
Storage	3,149,260
Spare Parts	139,702
Solvent (Water)	80,400
Solute (NaOH)	22,797,600
Catalyst	206,800,000
Electricity	1,184,000
Steam	6,465,600
Oxygen	18,763,690
Maintenance and repair	5,373,150
Labour (Operators, supervisors, lab work)	2,160,000
Staff overheads	1,512,000
Administration	378,000
Distribution and Sales	7,728,000
<b>TOTAL</b>	<b>274,739,786</b>



## 5 Results

### 5.1 Base Case

The following relevant outputs were determined from simulation, and are presented in Table 10:

*Table 10: Yields, purity, and recovery rates of vanillin during valorisation. The yield calculated by dividing final output of vanillin with fed lignin to the reactor. The vanillin conversion over the reactor is calculated by dividing output vanillin from the reactor divided by lignin fed to the reactor.*

	Vanillin
Yield	2.0%
Vanillin purity	99.9%
Vanillin conversion over the reactor	3.5%
Vanillin recovery succeeding the reactor	57.0%

Operating at an assumed 8000 hours a year, a maximum of 1024 tons of vanillin can be produced annually by the process design described above. As the worldwide market of vanillin is 20,000 tons [10], this would imply a market share of approximately 5%.

The total revenue of 154 MSEK is expected annually.

With the estimated economical life span of 10 years, an NPV of -1136 MSEK is obtained.

The unit operation costs and annual expenses involved in the calculation of NPV are summarised below in Table 11:

Table 11: Compilation of the unit operation costs and the annual expenses

Investment cost (bare module)	MSEK	Annual expenses	MSEK/year
Crystallizer	21.6	Catalyst	206.8
Membrane filtration	19.2	NaOH	22.8
Adsorption column 1	16.6	Oxygen	18.8
Adsorption column 2	13.4	Sales	7.7
Heater 2	6.7	Steam	6.5
Heater	4.4	Repair	5.4
Reactor	4	Storage	3.3
Dryer	1.8	Labour	2.2
Solid Filter	1.8	Filters	1.9
Washer	0.14	Staff	1.5
		Electricity	1.2
<b>SUM</b>	89.6	Admin	0.38
<b>Grass Root cost</b>	128.8	Spare Parts	0.14
		Water	0.08
		<b>SUM Operating cost</b>	-278.6

## 5.2 Sensitivity Analysis

A cost sensitivity analysis was made based function of catalyst recycle to investigate the effect on the NPV of the system. Two scenarios were addressed, one in which a greater proportion of catalyst can be recovered, and another were the ration of catalyst/feedstock was modified.

Figure 2 shows the significant effect that the recovery of the catalyst has on the NPV of the investment. As it is a major cost, reducing the amount of catalyst lost through a recovery system would be highly beneficial to the profitability of this process.

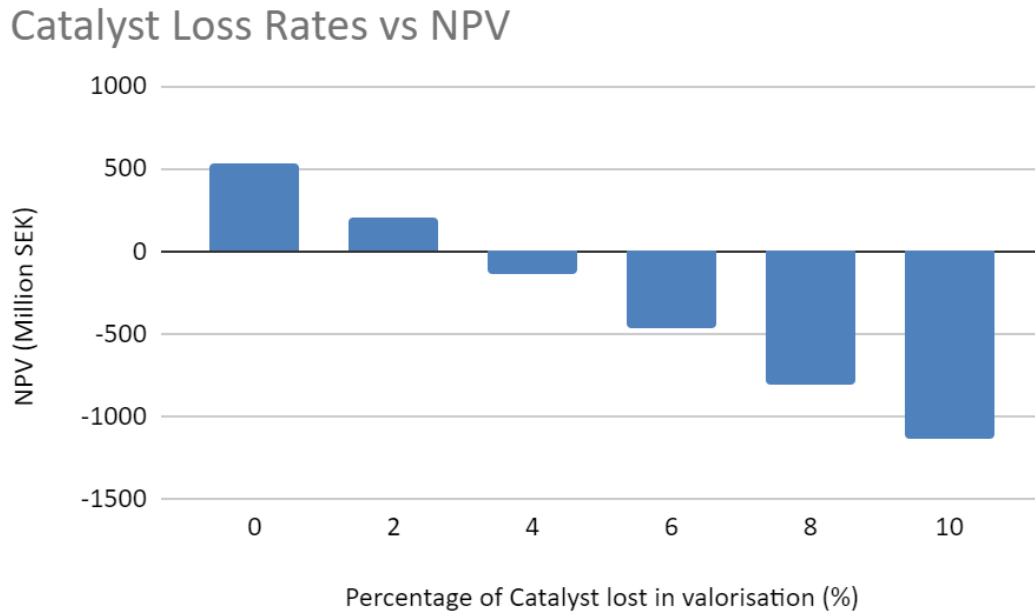


Figure 2: The effect of catalyst losses on the NPV of the investment. The base case assumes a catalyst rate of 10%/h, or a total of 517 tonnes/year.

Figure 3 reveals the effect of modifying the proportion of lignin/catalyst in the reaction. By reducing this to 1:40 catalyst:lignin, a positive NPV was achieved.

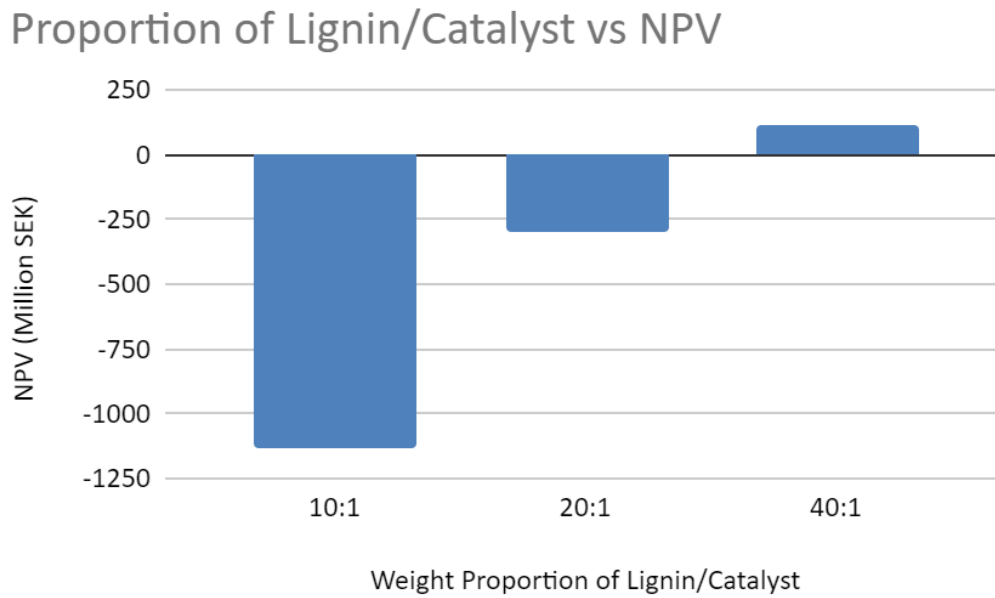


Figure 3: The effect that the proportion of lignin to catalyst has on the NPV of the system. The base case was assumed at a catalyst-to-lignin ratio of 1:10.

## 6 Discussion

One of the major assumptions made in this report was that only vanillin, vanillic acid, and acetovanillone were taken into consideration through the process. In reality a considerable proportion of the converted lignin would be by-products, such as carboxylic acids and other aromatics. This may impact the results, as obtaining high purity vanillin becomes simpler since there are less impurities to consider. This is observed in the report as 99.8% vanillin is already obtained at the filter press, which probably would not be the case with by-products present. The washer and the dryer were added to estimate an approximate cost for them as they would be needed for the plant and more research and equipment calibration would probably be needed when adding the by-products into the equation. The by-products could also present other problems, such as dealing with more complicated waste streams, handling of off-gases which will likely affect the profitability of the process.

Another thing worth noting is the type of lignin used as feedstock. As the product yields are greatly dependent on the feedstock, this could vary for the plant at Mörrum. In the report, yields from softwood kraft lignin are used but the feedstock at Mörrum is about one third hardwood and the rest is softwood. To further investigate this, a sample of the kraft-lignin could be tested in a small-scale reactor.

There is almost no known research about the purification of vanillic acid from such a solution and no research on other resins that could be used for adsorption. Solubility for vanillic acid in water was difficult to find, which makes a preliminary design of crystallization involve uncertainties since there was no laborations involved in this report. However, a standardized lab-test would probably be possible, and this should not be a restriction for future implementations.

VA should adsorb onto the resin, but since vanillin will have higher affinity and since our process is operating at a high pH, the vanillic acid might act as an ion [25]. What could be done is to investigate possible adsorbent resins, examine the possibility of ion-forming and in that case use an ion-exchange column or use an extraction method to recover the catalyst.

When it comes to the first adsorption column, one significant assumption is that the same total mass-balance over the column that is described by Gomes and Rodrigues [20], will be possible on an industrial scale. On the other hand, it could be that the efficiency at large-scale will be even better and what is the most probable is hard to speculate on. However, the design was based on experiments by Mota et al. [25], where vanillin at neutral pH was studied. That fact, together with the product mix that is produced from the reactor would imply different results regarding adsorption isotherms. Also, if there would have been more time, a more rigorous description of the adsorption column could have been made in programs, such as Aspen or COMSOL. Though it was considered that this relatively simple up-scaling method as described by Karlsson [24], would be reasonable for a feasibility study.

Since the adsorption columns were considered one of the remarkably expensive units in terms of investment, this was chosen to be designed in a more detailed way. However, there is still a large step going from these calculations into implementing a large-scale column. The uncertainty factors, such as competing adsorption between the three modelled compounds and the adsorption behaviour at such high pH should really benefit from a pilot-scale testing of a

depolymerised lignin-solution. The pilot testing could also help to estimate the desorption time as this is simply assumed to be equal to the adsorption time.

Moreover, most of the lignin out from the reactor would not be fully depolymerised. The simulations done in Aspen were already simplified as separator units were used and outgoing flows were specified for every unit besides the reactor, the heat exchangers and the pumps. It was however unavoidable for this report as more time would be needed to rigorously model an adsorption column, filters and the other units as these are rather difficult and complex to model in Aspen. The reactions occurring in the reactor were also stoichiometrically modelled as there were no known kinetic data available. Therefore, the energy and results from the reactor and the process may vary from an actual experiment.

After the filter press, the mixture of water, vanillic acid and acetovanillone could be separated for several uses. Firstly, acetovanillone could be further separated and sold as product. It can act as an active substance and has pharmaceutical uses and the estimated selling price is 2 000 SEK/kg. Since this could be an interesting product and income source, the possibility of purifying acetovanillone should be of interest in the future. Secondly, the water could be recycled and used to lower the required water for earlier steps. There is a huge amount of water present in this process, and an optimization of water use could be made through recycling.

The retentate from the membrane filtration is recycled back to the mill as it contains large amounts of lignin that potentially could be transferred to the evaporators. This is due to the relative high lignin concentration of 17 wt%, calculated through mass balances, and a pH above 13. However, it is important to emphasise that adding mass to the mill should not affect its chemical balance. Since the stream only contains substances that are present within the mill (except for the trace amounts of catalyst), this could potentially work. There also has to be an integration point out from the mill to our reactor where the sodium hydroxide could be returned.

An alternative to sending the retentate from the membrane filtration back to the mill could be to recycle it back to the reactor. But it is not known whether the remaining lignin can be valorised further or not, which is a subject for further research.

Without any pilot study, it is hard to determine how often the membrane filters must be changed, or whether backwashing can be implemented to remove fouling.

Regarding the energy analysis of this process, it was kept simple as the process itself is not very energy-intensive except for the reactor. For a feasibility study it is probably at an appropriate level since there are not many possibilities of heat integration, but for more detailed studies, Pinch Analysis could be investigated.

The catalyst is a major player when it comes to the profitability of the investment. In the base case where 10:1 lignin-to-catalyst ratio is used, the NPV comes out at -1136 MSEK. But with 40:1, the NPV becomes 115 MSEK. Although this has not been done before, it does not seem unreasonable that this would work. This might affect the yield negatively, but the sum of the parts might lead to a higher NPV and thus a more profitable process. The 10% loss of catalyst is quite substantial, but there can be solutions in order to decrease that number. Maybe an ion exchange resin can be used to adsorb the homogeneous catalyst to recover the metal ions.

## 7 Conclusion

From the economic analysis, it was found that it was uncertain if the process described in this report would have a positive net present value. The largest operational cost in the process is the loss of catalyst in the membrane filtration. If the recovery of the catalyst would be improved or alternatively a heterogeneous catalyst would be developed, the economics of the process could significantly be improved. Vanillic acid and acetovanillone, the two other products investigated in this report, have a large potential value to improve profitability if separated sufficiently. Further research is needed on optimising the various process variables to provide a sounder base of this biorefinery concept.

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## 9 Appendices

### Appendix A – Mass balances

Mass flow rates (kg/h)											Temperature (°C)	Pressure (bar)
Stream	Lignin	Water	Aceto- vanillon e	Vanilli n	Vanillic acid	Sodium hydroxide	Cataly st	Oxygen	Off- gases	Air		
1								2606.1			150	5
2							646.3				150	5
3	6462.5	248791.8				20678.4					25	5
4												
5	6023.0	248791.8	32.3	226.2	181.0	20678.4	646.3				150	5
6	6462.5	248792.8				20678.4					100	5
7	6023.0	248791.8	32.3	226.2	181.0	20678.4	646.3					
8											15	1
9												
10	6023.0	248791.8	32.3	226.2	181.0	20678.4	646.3				25	5
11	6023.0	248791.8	32.3	226.2	181.0	20678.4	646.3				25	8
12											25	8
13											25	8
14											25	30
15											25	30
12+15	5721.9	24879.2	3.2	22.6	18.1	2067.8	64.6				25	
16	301.2	223912.6	29.1	203.6	162.9	18610.6	581.6				25	1
17		30362.1									25	1
18	301.2	223912.6	4.5	60.9	147.5	18052.3					25	1
19											25	1
20											25	1
21		30362.1	24.6	142.7	15.3	558.3					18.7	1

22		30362.1	24.6	142.7	15.3	558.3					18.7	1
23		30362.1	24.5	13.9	15.3	558.3					25	1
24			0.08	128.8	0.05						25	1
25		26.7									25	1
26		26.4	0.08	0.05	0.05						25	1
27		0.3	0.008	128.8	0.005						25	1
28										78. 5	40	1
29		0.1								78. 5	32	1
30		0,14	0.008	128.8	0.005						32	1
31									2606		150	5