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Bachelor Research Project

Are Bio-Based Chemicals the New Gold Mines?

The Valorisation of the Phenolic Fraction of Pyrolysis Liquids to Bio-Based Chemicals

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results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature.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

Abstract: The chemical industry is still highly dependent on fossil resources. Just like other sectors in our society, the use of non-renewable sources is in need of a change towards sustainability. One bio-based alternative for obtaining both bulk and fine chemicals is the pyrolysis of biomass. An assessment of this process and the potential in terms of feasibility is of interest when searching for sustainable alternatives in the chemical industry. In order to evaluate this bio-based alternative, two techno-economic analyses were performed, based on the fast pyrolysis of pine wood. These analyses included a process selection stage, an Aspen Plus$^{\text{TM}}$ model and a cost estimation. The pyrolysis of 610 ton pine wood per year resulted into 50 ton per year of p-hydroxybenzaldehyde with a gross profit of about one million USDollar per year. BTX was produced with a 100% selectivity towards toluene, which gave rise to a number of other applications. Both the small and industrial scale were not profitable when toluene was priced at $0.80/kg. 144 million tons of pine wood resulted in 10 kton per year BTX/toluene with a loss of 38 million USDollars per year. The results of the p-hydroxybenzaldehyde production indicate that the pyrolysis of biomass has potential to deliver intermediate compounds and to eventually obtain high-value end products. This study can show an insight into the technological and economic potential of chemicals from the pyrolysis of biomass.

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1 INTRODUCTION

On April 8 2020, the energy company Vattenfall received word that after years of discussions and evaluations, a permit has been granted to build the biggest biomass power plant of the Netherlands in Diemen, close to Amsterdam. In this plant, imported wood pellets are burnt to provide heat. The location of the power plant will be on the old site of two natural gas power stations. The company recognises that the pyrolysis of biomass for energy is just a temporary solution and that more renewable heat sources have to be developed over the years to replace the burning of biomass. [1]

Keeping our houses warm is not the only thing that is originally done with the use of non-renewable sources. For example, most bulk chemicals are still produced from petroleum. About 15% of an oil barrel goes to the production of chemical products. This seems like a small fraction, but those chemicals make up for about half of the profits. [2] Those bulk petrochemicals are important precursors for many chemicals and are present in our daily life products. However, the production of these chemicals is not sustainable and is responsible for one fifth of the total industrial greenhouse gas emissions [3].

Just like the transition from natural gas towards a more sustainable alternative, biomass can also be a solution for producing bulk chemicals. The demand for these bio-based chemicals is expected to grow more and more over the next decade. And when the demand is higher than the supply, the costs of these bio-based chemicals will rise. This could imply that there also is some sort of economic feasibility for producing bio-based chemicals in a more sustainable manner [4]. The pyrolysis of biomass, from waste to other non-food types of biomass, yields both fuels and energy, as well as the bio-based chemicals [5]. Depending on the pyrolysis technique, one of these three products is often favoured [6]. At this moment in time during the COVID-19 crisis, the oil prices are historically low due to the decreased demand. But also in normal times, competing with petrochemicals is very hard for the bio-based industry due to the significantly higher costs of production [7], [8]. Policy makers have a duty in this area towards the climate and the benevolent sustainable companies to provide more tools to improve techniques and extent the company's reach.

More consumers are aware of climate change and the role of their behaviour on the greenhouse gas emissions. They turn more and more towards sustainable alternatives, causing an increase in the demand of those bio products. This change towards a more sustainable society is also noticeable in companies. More than 90% of the CEOs state the importance of sustainability for their companies success [9].

This rising awareness is often limited. Consumers are unaware that the plastic around their newly purchased laptop originates from fossil resources, let alone the origin of the other compounds inside the device. Therefore, the industry should take their responsibility to change the way chemicals and materials are produced. Hence, researching the possibilities of obtaining chemicals from bio-based sources, like from the pyrolysis of biomass is important and interesting to do in this changing world. In this work, this is done by first doing a small background study about the pyrolysis of biomass, the fractionation of the products and the main study about the potential of the major components in the phenolic fraction: cresol and creosol.

The main question is stated as follows: *What is the technological and economical potential of the phenolic fraction obtained from the pyrolysis of biomass for the synthesis of individual high-value chemicals?*

The expectation is that there will be technological potential for the compounds, since there is a lot of research available on conversion routes and optimization processes. However, this abundance of information could make it harder to find relevant sources. Several sources show promising processes which can be used for the process design. The economic potential is, as mentioned, difficult for bio-based sources due to the high production costs. Therefore it is expected that the economic feasibility of the selected conversion routes will not be comparable to the products obtained from petrochemical sources.

This work will show some possibilities into obtaining high-value compounds from bio-based sources. The exact conversion routes might need more extensive research. However, reading and evaluating this work might help creating a mindset that it is possible to extract chemicals from the product of biomass pyrolysis, which can be converted into compounds that are now made from non-renewable resources.

2 BACKGROUND

2.1 PYROLYSIS

Pyrolysis is defined as the thermal degradation of organic compounds without air or oxygen at elevated temperatures [10]. Biomass is often used as feedstock and can be obtained from various sources, which will be discussed later on. The products of pyrolysis can generally be divided into a solid, liquid and gas phase. The liquid and gas phase mainly consist of volatile matter (aromatics for example). The solid phase consists almost completely of charcoal. The pyrolysis process can thus generally be described with the following general reaction:

$$\text{Biomass} \longrightarrow \text{Charcoal} + \text{Volatile matter} \quad (2.1)$$

After the pyrolysis reaction is done, the three phases are often separated due to their different end-uses. The charcoal can be separated from the volatile matter because of its solid form. Some of the volatile compounds are condensed to become a liquid, which is subsequently separated from the remaining gas phase.

Currently, there are three main techniques used for the pyrolysis process: slow, fast and flash. Those processes are different in terms of residence time, temperature and heating rate. Some of those characteristics can be seen in Table 2.1. From this table it is visible that the liquid yield differs with the technique used. Slow pyrolysis is mainly used to obtain a high yield in solid char, whereas both fast and flash pyrolysis are mainly focused on achieving a high amount of pyrolysis liquid with the lowest solid content as possible. The applied method will obtain the desired product in the highest yield when applying the corresponding process conditions. The main difference between those three methods is the residence time of the solid phase.

The total liquid yield of the slow pyrolysis product mixture is small. However, some components in the pyrolysis liquid are in higher weight fractions present when slow pyrolysis is performed, if compared with the other types of pyrolysis. One example of this phenomenon that is relevant to mention is the high weight fraction of liquid ester compounds in the slow pyrolysis product mixture [11], [12]. This shows that the choice for either slow, fast or flash pyrolysis is not always straightforward. The product distribution of flash pyrolysis can be compared with fast pyrolysis. The main advantage of this method compared to fast pyrolysis is the fact that the shape and size of the feed particles is less important for flash pyrolysis. Therefore, a larger variety of biomass resources is available [11].

Many mechanisms and reactions have been proposed for pyrolysis, almost all different due to the variation in the composition of the biomass sources. Figure 2.1 shows a scheme which is an example for the reaction pathway of fast wood pyrolysis, based on research from Venderbosch and Prins [13] and Koido and Iwasaki [14].
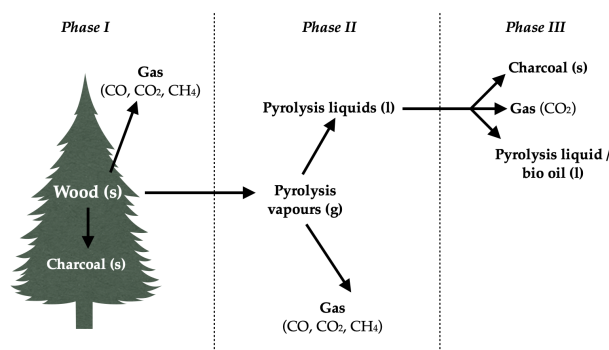
Figure 2.1: Schematic overview of wood pyrolysis, based on [13], [14]

Phase I can be seen as the stage in which the primary phase decomposition takes place and already a separation between solid (char), non-condensable gas and condensable pyrolysis vapours. Those primary decomposition reactions take place at temperatures around 200 to 400 °C. This relatively low temperature has as consequence that some groups such as the aromatic methoxy groups are still stable during this primary stage. Therefore, the reaction products after the first pyrolysis stage often include 4-substituted guaiacols or syringols.

	Temperature range (°C)	Heating rate (°C/s)	Residence time of solid phase	Liquid yield (wt%)
Slow	550 to 700	0.1 - 1	Days	30
Fast	450 to 550	10 - 200	Minutes/hours	60 - 80
Flash	800 to 1000	> 1000	< Seconds	65

Table 2.1: Overview of the pyrolysis processes, based on [6], [11], [15], [16]

The second decomposition reactions (see phase II in Figure 2.1) are at elevated temperatures of about 400-550 °C. This causes a transformation of the guaiacols and syringols to catechols and pyrogallols [17]. The temperature of this stage corresponds with the earlier mentioned fast pyrolysis temperature range in Table 2.1. In this pyrolysis step, compound groups called cresols and xylenols are also formed [18]. The pyrolysis vapours can be separated and partly condensed in the second phase into a liquid fraction, the pyrolysis liquids, and gases. Those pyrolysis liquids obtained in the second phase are often called intermediate bio-oils and still contain quite some solid char.

Because of the difficult and extensive separation of those particles, the intermediate bio-oil is not always purified inside the same plant as the pyrolysis. It can be sold in crude form to other plants which are able to perform additional separation or have a direct usage for the crude material [19]. In phase III (Figure 2.1) this step is shown by separating the remaining gas (mainly carbon dioxide) and the solid charcoal particles from the pyrolysis liquid, generally resulting in a liquid weight fraction in the range of 50-80% for the process of fast pyrolysis [6]. It should be stated that the described process is simplified since pyrolysis in reality consists of multiple reactions occurring at the same time [15].

Besides a description of the process and its possible mechanisms, it is also important to discuss the type of feedstock for pyrolysis. It was already mentioned that the most common feedstock is biomass. There are a lot of possible biomass sources which can be converted by pyrolysis into a product mixture with the desired fractions based on the applied process conditions. Some examples of biomass sources are agricultural residues such as pits, wheat or rice straw [11] and wood like pine wood or hardwood. Besides the type of wood, there are multiple ways in which wood is processed before it enters the pyrolysis process [15]. The following processing products are available, respectively from large to small particle sizes: bark chips, pellets, shaving and sawdust [20]. The particle size of the feedstock also plays an important role in the pyrolysis, since biomass has a low thermal conductivity. So when fast or flash pyrolysis is desired, the heat transfer from a heat source to the biomass should be high in order to be able to provide the correct heating rates. Small particle sizes show

better heat transfer and are therefore preferred in fast and flash pyrolysis. [21]

Biomass generally consists of three main components: cellulose (15-49 wt%), hemicellulose (12-50 wt%) and lignin (6-30 wt%) [22]. Depending on the type of biomass, the weight fractions of each of those three compounds in the biomass source differ [6]. This difference in composition results in significant differences in the pyrolysis product mixtures. One relevant example that shows the influence of the biomass composition is the composition of the phenolic fraction in the pyrolysis liquid. The major phenolic compounds in this fraction include guaiacols, phenols and syringols. Those compounds are mainly derived from lignin. During pyrolysis, lignin will thermally decompose into these phenol derivatives [23], [24]. Therefore, a higher lignin content in the biomass will also increase the yield of these phenolic compounds. Another example is the research of Oyebanji et al. [15], they came to the conclusion that biomass samples with a relatively high ash content are not suitable for the production of pyrolysis liquids. Ash will catalyse the cracking of the pyrolysis liquid to gasses, which results in a product loss.

So not only the parameters mentioned before such as heating rate, temperature and residence time are things that should be paid attention to when performing pyrolysis. The biomass source also has a significant influence on the weight fractions of the compounds in the product.

In order to obtain the desired fractions and chemicals of the pyrolysis liquids for applications, separation steps should be taken in order to separate the defined fractions. This is discussed in the following section.

2.2 FRACTIONATING PYROLYSIS LIQUID

Firstly, it is important to define the fractions present in pyrolysis liquids in order to propose fractionation possibilities. The pyrolysis liquid will generally appear as a two phase system. The two phases are a water soluble aqueous phase and a water insoluble oil phase. There are more than 400 compounds present inside those two phases. Due to this immense amount, it was not possible to take into account all these compounds in this report. Therefore, only the most abundant chemicals and functional groups are discussed.

The aqueous phase consists of chemicals such

as acetic acid, acetone and methanol, whereas the non-aqueous phase consists of heavy molecules such as oligomers or polymers and mainly aromatics. This phase has the potential to substitute fossil fuels. Presumably, this is done by a partly substitution of the fossil fuels in combination with the biomass based aromatic phase. This thus means that there is still a fraction fossil fuels left in the fuel product [25]. The aromatic compound groups that are most present in this lower phase are guaiacols, phenols and syringols. The aqueous phase has a higher water content in which sugars and other non-aromatic compounds accumulate. [12]

A more specific classification of the pyrolysis liquid can be done by looking at the functional groups of the components present in the liquid. The extensive review on pyrolysis liquids published in 2019 by Pires et al. [26] divided bio-oil into five main fractions, shown in Table 2.2. These values match with the data of the bio-oil obtained from (pine) wood biomass sources researched by Thamburaj [27], Sipilä et al. [28] and Zhang et al. [29].

	wt%
Water	15 - 30
Light oxygenates	8 - 26
Monophenols	2 - 7
Water insoluble oligomers derived from lignin	15 - 25
Water-soluble molecules	10 - 30

Table 2.2: Main Fractions of Pyrolysis Liquid [26]

As mentioned previously, the ratio of compounds in those pyrolysis liquids differs with the biomass composition and especially due to the different weight fractions of the three main components (cellulose, hemicellulose and lignin). For example, biomass sources with a higher lignin fraction often result in more phenolic compounds [12]. That is why the weight fractions in Table 2.2 are in a large range.

Venderbosch and Prins [13] wrote a specific article about the fast pyrolysis of biomass, including the chemical composition of the pyrolysis liquid obtained from the pyrolysis of pine wood. Table 2.3 shows the weight fractions of the fractions. The major compound that is part of the fraction is in brackets behind the corresponding fraction. In order to provide some sort of assessment of whether this data can be used further on, the values are compared with Table

2.2. This comparison shows that the values of Venderbosch and Prins [13] are in the range of the general weight percentages based on the data obtained by multiple other researchers. Therefore, the data from Table 2.3 is considered to be representative and relevant, and is thus used in this research as pyrolysis data source.

	wt%
Water	23.9
Sugars (levoglucosan)	34.44
Aldehydes and ketones (furan)	15.41
Guaiacols, catechols and phenols (cresol)	13.44
Extractives	4.35
Acids (acetic acid)	4.3
Alcohols (isopropanol)	2.23
HMM lignin	1.95

Table 2.3: Composition of the liquid fraction [13]

The composition of the fractions present in the pyrolysis liquids are now clearly stated. Subsequently, the different options for the separation of those fraction and its compounds are considered. The main focus for the separation techniques is the separation of the phenolic fraction. The reason for this is the focus of the following part of the research, namely the application of specifically the phenolic fraction and some of the compounds in it.

One way to fractionate the pyrolysis liquid is already partly discussed, namely by performing only the primary decomposition reaction from Figure 2.1 in a certain temperature range [30]. This prevents the formation of secondary decomposition products. An increase in pyrolysis severity is another option for the fragmenting of the pyrolysis liquid during pyrolysis. This is done with a higher temperature and heating rate. This causes the cracking of most compounds containing an unstable oxygen atom, which reduces the organic liquid yield but also leaves less oxygen containing compounds in the pyrolysis liquid [31]. Those two fractionation methods influence the composition of the fraction since the pyrolysis can be regarded as not completed, based on the three defined phases. This is due to the fact that the data previously shown, such as the product composition, is based on a completely performed pyrolysis process.

Possibly the simplest method of rough fractionation when the whole pyrolysis process is performed according to the earlier described method

(and Figure 2.1), is the separation into two fractions based on water solubility. The water soluble compounds with mainly carbohydrate derivatives will form an aqueous top layer, whereas the more heavy viscous fraction will settle at the bottom. The aqueous layer can be extracted from the viscous fraction with as result a purified viscous fraction. This fraction will mainly consist of aromatic, oligomeric and polymeric compounds [31]. The aqueous fraction contains compounds with functional groups such as aldehydes. The phenolic fraction can either be present in the viscous fraction due to its aromatic functionalities, or the fraction will dissolve in the aqueous phase when an alkali substance is added [28], [32], [33].

The traditional method for the separation of the phenolic fraction from pyrolysis liquids starts with adding a strong alkaline aqueous solutions (such as NaOH), which causes a reaction from phenols to phenolates. The two phase system is now in equilibrium and the apolar oil-phase is enriched with phenolics and lignin derivatives. The aqueous phase contains mostly acids, alcohols, aldehydes, sugars and the phenolic fraction in the form of phenolates. An extraction can be performed to separate the organic phase with for example hydrocarbons, from the aqueous phase. Subsequently, the phenols can be extracted from the aqueous phase by acidification with mineral acid (HCl). This phenol extraction with a yield of 95% is shown in Figure 2.2.
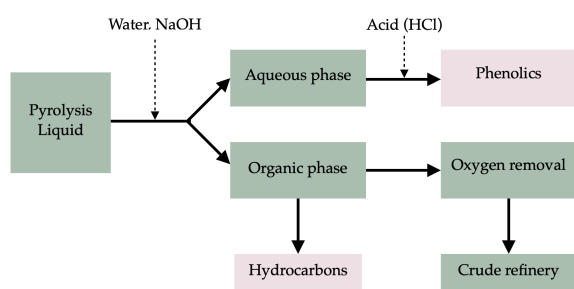
Figure 2.2: Fractionation of the phenolic fraction, based on [32], [33]

In order to improve the extraction of the phenolic fraction from the pyrolysis liquid, an alternative but comparable method is also available from the company DSM [34]. They propose a multiple step extraction of phenol from the pyrolysis liquid by adding water and a solvent. Firstly, acetic acid will be extracted, followed by a hydrodeoxygenation in which all oxygen will be removed from compounds containing oxygen. After that, the phenol related compounds can be removed and the remaining bio-oil is upgraded.

The company BTG also has some extensive fractionation methods, in which the pyrolysis liquid is fractionated based on the end-use. The fractionation will thus result in various qualities of pyrolysis liquid which can be further upgraded into energy, fuels or chemicals. The pyrolysis oil is first separated into pyrolytic lignin, pyrolytic sugar and a watery phase containing mainly organic acids like acetic acid, see Figure 2.3. Compounds derived from lignin are mostly present in the pyrolytic lignin, whereas sugars such as levoglucosan and larger sugar molecules are concentrated in the pyrolytic sugar. [35]
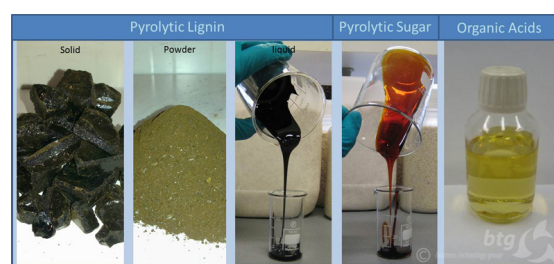
Figure 2.3: Fractionation products [35]

A lot of other innovative research has been done on the extraction methods of the phenolic fractions, for example with supercritical carbon dioxide [36] or so-called phenolic distillation [37]. Those studies all resulted in the extraction of the phenolic fraction and all have in common that the phenols are isolated as one fraction.

For the next part it is assumed that the phenolic fraction is now separated from the other fractions in the pyrolysis liquid. The next step is to evaluate the applications of the whole fraction and subsequently of the individual compounds present in this fraction.

2.3 APPLICATIONS OF THE PHENOLICS

Some of the phenolic compounds are known to act as insectides and fungicides. Therefore, one application of the phenolic fraction is in wood as a preservative. However, the efficiency of adding this in wood was short-lasting according to the latest research [31], [38]. If this lifespan could be improved, the fraction could be used as an environmentally friendly wood preservative.

The phenolic fraction can also be used as a binder for multiple purposes. One example is the research for using the liquid phenolic fraction as a partial replacement for asphalt binder (fossil bitumen) [39], [35]. Besides this type of binder, it can also be used in wood composite products. In

order to perform as a binder, the pyrolytic lignin has to transformed into a resin. A representative synthetic resin is the phenol-formaldehyde (PF) resin, which is formed by the reaction of formaldehyde with phenol or substituted phenols [40]. It seems that pyrolytic lignin has the potential to replace fossil phenol. However, there are still quite some technical hurdles to overcome. For example, the liquid has a low reactivity since it is a mixture of phenolic compounds and it is not a pure compound [40]. The research of Sukhbaatar et al. [41] showed that a replacement of the phenol-formaldehyde resin with the bio-based phenolic resin is more or equally effective up to about 40% replacement for the synthesis of wood adhesives. More recently, Chaouch et al. [42] researched the same and also proved that the performance was comparable or even better than the pure phenol-formaldehyde resin up to 50% incorporation of the bio-based phenolic resin. Phenol can also be substituted up to 75 wt% with the pyrolytic lignin from BTG and still meet the standards for that type of resin [35].

Some applications of the bio-oil fractions were already known 25 years ago in the food flavouring industry. The water-soluble part of the pyrolysis liquid with the low-molecular weight aldehydes are meat browning agents. The phenolic fraction also has a function in this same industry because it provides smoky flavours [31].

The previously mentioned applications are based on the entire phenolic fraction. However, there are a lot of individual and valuable chemicals present in this fraction. The major compounds in the phenolic fraction include the previously mentioned guaiacols, phenols and syringols, mainly derived from lignin. Some of the phenolic compounds are also present as oligomers, which will accumulate in the water-insoluble fraction [31]. An application is to recover some of the useful phenols from the pyrolysis liquid. Those chemicals can then in turn be used for various applications. However, it is difficult to separate the individual phenols from

the phenolic fraction due to the fact that these compounds are similar to each other and often present in small amounts (< 2-3 wt%) [2], [40]. The costs of this separation are high, so in order to make this cost efficient and commercial, more research should be done [31].

Even though the costs of the separation are often high and the efficiency is low, there are some studies about separation techniques with the goal to separate the phenolic fraction into either different components or different functional groups. One recent research about innovative techniques is done by Mante et al. [43]. The basis of their technique is a combination of solvent extraction, distillation and separation based on the acid strength of the components. Figure 2.4 summarises the separation process of monofunctional methoxyphenols with a final purity of about 86.3 wt%. The methoxyphenols in the product and the final compositions after the separation steps are shown in Table 2.4, together with the corresponding boiling points. These boiling points indicate that further separation, for example by distillation, will be difficult.

	Composition (wt%)	Boiling point (°C)
Eugenol	7.5	253
Isoeugenol	33.9	254
Guaiacol	7.2	205
4-methylguaiacol	18.7	221
4-ethylguaiacol	10.9	235
4-propylguaiacol	13.8	264

Table 2.4: Methoxyphenol composition and boiling points [44], [45], [46], [47]

Some of those phenolic compounds, like eugenol, guaiacol and isoeugenol have a relatively high market value compared with the cresols [48]. Therefore, in order to make the cresols more valuable, conversion routes can be investigated to other more valuable compounds, which is done later on in this study. First, a quick process design is performed of the until now described process.
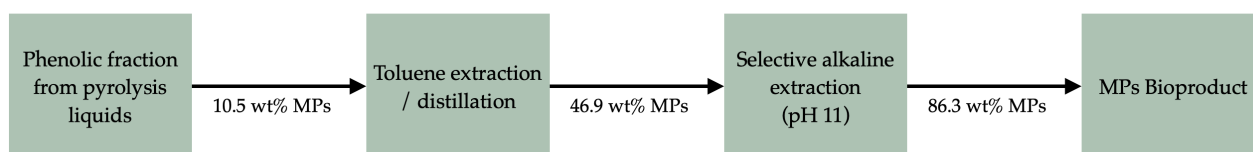
Figure 2.4: Overview of the separation steps and weight percentages methoxyphenols (MPs), based on [43]

2.4 Process Design Fast Pyrolysis

So, all things considered, when the goal is to obtain either the phenolic fraction or chemicals inside the phenolic fraction, the first choice that should be made is the biomass feedstock. A biomass source with a moderate to high lignin composition will result in a higher phenolic fraction yield. This is the case with the previously mentioned research of Venderbosch and Prins [13], in which pine wood is the feedstock. The type of pine wood was chosen to be sawdust with small particle sizes [20]. This will aid the heat transfer from the heat source to the biomass particles [21]. The pine wood sawdust is then treated with the fast pyrolysis process and the reaction conditions according to Table 2.1. This process was chosen because in this way, the highest liquid yield could be obtained. The first separation is based on the different phases that are present in the pyrolysis product. Subsequently, the phenolic fraction can be separated from the other fractions in the pyrolysis liquid by either the process of DSM or that of the company BTG, since the two processes seem to be equally effective and already functioning on pilot plant scale. The next step is to isolate the methoxyphenols from the phenolic fraction. This is done by extraction and distillation after which the methoxyphenols end up in a purity of 86.3 wt%. A block diagram, Figure 2.6, was made of the overall pyrolysis process and separation steps.
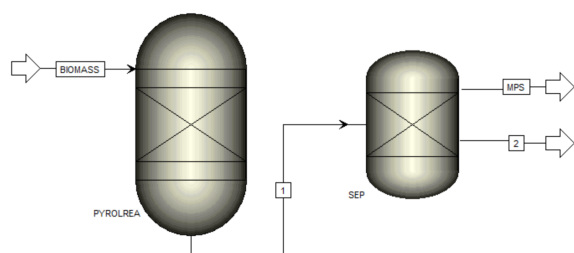
Figure 2.5: Aspen Plus™ model of pyrolysis

A yield reactor was used to be able to model the different mass fractions from Table 2.3 [13].

It is important to define the costs of the pyrolysis process. This is also useful for the cost estimation that will be constructed later on with pyrolysis as basis. The previously mentioned company BTG (Biomass Technology Group), located in the Netherlands, has a commercial scale demonstration of the fast pyrolysis of biomass with parameters corresponding to the ones mentioned in this project [49]. For example, the biomass feedstock was wood with a small particle size, just like the pine wood sawdust selected for this process. The results of the BTG design are shown in Table 2.5.

Capacity of biomass conversion	5 ton/hr
Biomass costs	€80/ton
Production Pyrolysis liquid	3.2 ton/hr
Cost Breakdown	
- Biomass feedstock	43%
- Personnel	10%
- Other variable costs	3%
- Other fixed costs	2%
- Finance costs	42%

Table 2.5: Plant Design by BTG [49]

The useful things from this table are mostly the yield of actual biomass conversion to pyrolysis liquid and the cost breakdown. This table shows that the biomass feedstock costs are about 43% of the total pyrolysis process costs The biomass feedstock costs can be calculated with the designed process, since the amount and price of the feedstock ($77/ton, corresponds approximately with the mentioned €80/ton) are known. So, the total costs of the pyrolysis can be calculated.

In the following sections, two compounds in the phenolic fraction of pyrolysis liquid, cresol and creosol, are discussed. The focus on those two is based on the previously mentioned relatively low market value compared with the other phenols.

Figure 2.6: Block diagram of the pyrolysis process

2.5 CRESOL

Cresol can occur as three isomers due to the ortho, meta and para positions of the methyl group (Figure 2.7). All three isomers are present in pyrolysis liquids if fast pyrolysis is performed [50]. This mixture of stereoisomers is called cresylic acid [51].
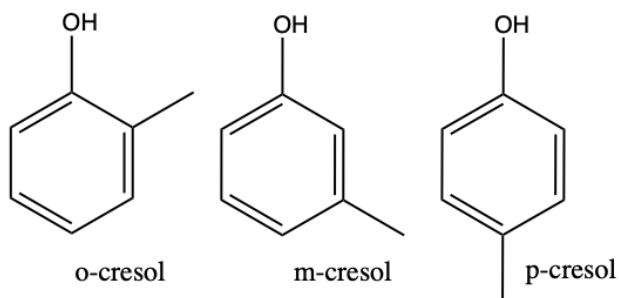
Figure 2.7: Cresol isomers

Cresols occur naturally in plants and food and are also produced in mammals by metabolism [52]. In 2010 the global consumption of cresols was 223.4 kton and has grown in recent years to a total of about 274 kton. 90% of the applications of the cresols are as chemical intermediates in resins, pesticides, dyes and antioxidants. Much smaller amounts of cresols are used in disinfectants, flavouring agents and pharmaceuticals. Most of these applications are for the separated cresol isomers. Applications of the cresylic acid mixture lie in the automotive and the food packaging industries. [52]

As mentioned, cresol is mostly used as intermediate, meaning that the compound is generally reacted further to other compounds of interest. It is important to state that most of these conversion routes are specific for one cresol isomer. This is a difficulty when cresols obtained from the pyrolysis liquids are used, since the pyrolysis process only yields cresylic acid. The separation of those three isomers is studied in detail already from the 1950's up until now ([53], [54], [55], [56]). The ortho isomer can be separated relatively easily from the other cresols by distillation [51]. This separation could be an additional separation step that has to be added in the process. However, there is no reported research about the process steps to other compounds with regards to using a mixture of isomers instead of a pure isomer. It is thus unknown what the effect of this would be. There are also some articles published about isomerization routes of the cresols [57], [58]. So if the cresols are able to be separated, they can be converted to the desired isomeric form.

2.6 CREOSOL

Creosol is also often called 4-methylguaiacol or 2-methoxy-4-methylphenol. It almost has the same applications as cresol, namely as intermediate in the synthetic and pharmaceutical industry or as end-use in the food and perfume industry. It is used as flavouring

Figure 2.8: Creosol

substance, most common in beverages and chewing gum. [59] It occurs naturally in mushroom, coffee, whiskey and some flowers [60].
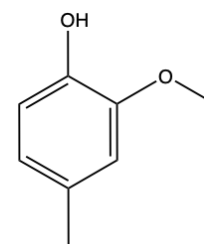
3 METHODOLOGY

As mentioned at the end of Section 2.2, cresol has a lower market value than other methoxyphenols present in the final mixture and the main application is as intermediate for different industries. Therefore, it is logical to look further at possible conversion routes of cresol to high-value compounds instead of immediately using the compound. So the next step was an assessment of possible conversion routes.

It should be noted that this literature search into the conversion possibilities was performed in a certain time frame and the results will therefore not show all the possible conversion routes that are available and known over the world. This selection was made on already a quite in depth search of scientific literature. However, there will of course be other conversion routes possible that are not considered in this analysis.

All products from the conversion routes of cresol and creosol are evaluated in terms of application, now and in the future, based on literature sources. Since the idea is to eventually design a process of the chosen product, it is important that the product has a future perspective and this is evaluated, and taken into consideration when making a choice.

After this first selection of products that can be obtained from cresol and creosol, there were still a lot of options with some interesting applications. Therefore, some other criteria were specified in order to make a well-advised choice. The products were all rated on a scale from 1 to 5 according to the twelve green chemistry principles [61]. In this case, 1 is given when the prin-

ciple is not pursued in the conversion route or product, and 5 when the principle is completely pursued and applied. Besides the grading for the green chemistry principles, two other boxes were added with the application (1 is no application, 5 is a huge range or important applications) and the costs (see Table 3.1) of the product. Since a lot of different prices can be found based on the purity, a general purity of 99% was taken as reference price. This method was chosen to guarantee a good and equal comparison of the conversion routes. The average grade is calculated by treating every green chemistry principle equally important and doing this as well for the application and cost.

Number	Value
1	$\leq$ €100
2	$\pm$ €150
3	$\pm$ €300
4	$\pm$ €500
5	$\geq$ €1000

Table 3.1: Cost evaluation (per kg product)

With those results, two conversion routes and products were elaborated in a process design and an analysis. This included a detailed theoretical process description based on literature on this specific reaction and process. This consists of the description of the reactions occurring, the catalysts and solvents used, the design of a block diagram and defining the reaction conditions. Subsequently, this theoretical process was modelled in Aspen Plus™ with the values found in literature. This will be further explained in Section 3.1. The goal of the model was not to completely mirror the theoretical process but to obtain relevant and representative data. A couple of assumptions were made in order to be able to design the plant in the best way as possible. Some of the reaction conditions of the separation steps were optimised in order to obtain a product with a higher purity. Examples of these optimised parameters include the ratio of recycle to purge stream and varying the temperature and pressure of, for example, a crystallisation or distillation step. The most optimal conditions, based on the mass flow/fraction of the final product stream, were chosen as conditions for the final model.

Based on the results from the lab scale model, a cost analysis was made. The costs were estimated by using the methods according to Towler and Sinnott [62], a more detailed description is given in Section 3.2. After this, the process was scaled up to more industrial scale. The chosen capacity was based on some already existing plants and the market size. The process was modelled in Aspen Plus™ and, if applicable, optimised with the previously mentioned parameters. The data obtained from this model was used for another cost estimation based on the same method as for the smaller scale. Subsequently, a comparison could be made about the two scales and conclusions could be drawn about the technological and economical feasibility of the plant. This was done for two compounds in the same manner.

The first part of the cost estimation was based purely on the conversion from cresol or creosol to the chosen product. However, it is important to also take the pyrolysis process into consideration in order to be able to perform a representative cost estimation, since the whole idea is based on the idea to obtain products from the chemicals obtained from the pyrolysis of biomass. Therefore in order to provide a clear economical analysis whether the pyrolysis of pine wood to cresol/creosol and eventually to the products is feasible, data from the previously mentioned company BTG was used [49]. The costs of the pyrolysis process are estimated by using the percentages provided in Table 2.5. This means that the pine wood sawdust price per year was considered to be 43% of the total costs.

The amount of pine wood necessary for pyrolysis to provide enough cresol for the reaction was based on the previously mentioned data. This concluded that the yield of the pyrolysis of pine wood to pyrolysis liquid was between 60-80 wt%, and 64 wt% according to BTG [49]. Therefore 64 wt% was used as yield. Section 2.2 also mentioned a fractionation yield of 95%, which will also be taken into account. The cresol fraction inside this pyrolysis liquid was considered to be 13.44 wt%, according to Table 2.3.

3.1 ASPEN PLUS™ SIMULATIONS

The base method was set to the activity coefficient-based property method NRTL. This method is chosen because the simulation operates at pressures less than 10 atm and without near critical components [63]. When the situation occurred that no parameters were available of a compound, an isomer of this compound is chosen to represent this chemical. Therefore, the assumption is made that this is possible and will not significantly affect the results. The specifi-

cations of the different equipment pieces were filled in according to the reaction conditions from the articles used as reference. The same is done for the components, the ratios of the compounds were taken to be the same as the experimental values from the consulted sources. Catalysts were not added in the simulation since they do not participate in the reactions.

Recycle streams were attached to the model, if applicable. A purge stream with a splitter is added before attaching the recycle stream to avoid accumulation. This purge stream was initially set to a purge recycle ratio of 1:9. If this did not give any problems and the feed stream of the recycled compound could be lowered with the same results, the purge recycle ratio could be optimised in order to recycle more.

Significant pressure and temperature changes were modelled by using respectively a pump or compressor and a heater or cooler. When a stream was mainly vapour but consisted of a small part of liquid, both a pump and a compressor had to be added after a gas/liquid separator. If this was not done, errors would occur and the model would not function properly. It is of course important to realise that this would work different in a real plant. A special flash column (Flash2) could model a gas/liquid separation, whereas a decanter was used for a liquid/liquid separation. Liquid/solid separation was performed with a centrifuge (CFuge) in which the solid load of liquid outlet could be specified by trial and error. The model was not able to operate when the value was set too low. When this occurred, the program gave as solution the minimum value it should have, which was then used as new input. The DSTWU shortcut distillation model was applied for distillation processes.

3.2 COST ESTIMATION

3.2.1 EQUIPMENT COSTS

The equipment costs were estimated with the purchased equipment cost model from Towler and Sinnott [62]. This method uses correlation of costs constants with the size of a parameter, specified for each equipment type. The formula to calculate the purchased equipment cost is shown in equation 3.1 and is based on the U.S. Gulf Coast (January 2010).

$$C_e = a + b\,S^n \tag{3.1}$$

In this equation both a and b are cost constants, S is the size parameter and n the exponent for a type of equipment. All equipment had a minimum and maximum S value, meaning that for small scales the minimum S value was often used, since the actual value for this parameter was way below this minimum.

3.2.2 CORRECTION AND OTHER COSTS

The equipment costs calculated with equation 3.1 were based on the period January 2010. To make those values more accurate and current, the Chemical Engineering Plant Cost Index (CEPCI) can be used to update those costs. Unfortunately, the latest freely available CEPCI value was published in 2018 (603.1) [64].

$$\text{Costs 2018} = \text{Costs 2010} \times \frac{\text{CEPCI 2018}}{\text{CEPCI 2010}} \tag{3.2}$$

The so-called inside battery limits (ISBL) investment, or also known as the cost of the plant itself, is then calculated by applying the Lang Factor. This factor is an installation factor which estimates the costs besides the major equipment costs. A Lang Factor (F) of 3.63 was chosen when the plant was a mixed fluids-solids processing plant [62]. The OSBL investments are other costs that include modifications and improvements to the infrastructure of the plant site. The value of this differs per plant and is calculated as percentage of the ISBL costs. For the a small scale, 20% was a good value, whereas for a more industrial scale the more generally used 40% was applied. This percentage is often used as initial estimation when not much of the details are known. The engineering costs and the contingency costs are also part of the total fixed capital cost and are respectively 10% and 15% of the ISBL plus OSBL costs. The total fixed capital costs are calculated by adding the ISBL, OSBL, Engineering and Contingency costs. Additionally, the working capital is assumed to be 5% of this total fixed capital cost. The costs of the utilities are assumed to be dependent on the size of the plant. For an industrial scale, the utilities were estimated to be 10% of the so-called Cash Cost of Production (CCOP), whereas for a smaller scale, 2% was assumed. An overview of inputs for the cost analysis is shown in Table 3.2.

Another important cost for a sustainable plant is efficient waste treatment. Aqueous waste is considered to be the biggest waste fraction in the

designed plants. In order to cover for these expenses, per kg aqueous waste $1.50 is paid [62].

There are more fixed costs, namely the fixed operating costs. For estimating these costs, a template of Towler and Sinnott was used [65].

CEPCI Jan. 2010	532.9
CEPCI 2018	603.1
Lang Factor	3.63
OSBL: small scale	20% of ISBL
industrial scale	40% of ISBL
Engineering costs	10% of ISBL+OSBL
Contingency	15% of ISBL+OSBL
Total fixed capital costs	ISBL + OSBL + Engineering + Contingency
Working capital	5% of total fixed capital costs
Aqueous waste	$1.50 per kg
Utilities small scale industrial scale	2% of CCOP 10% of CCOP

Table 3.2: Overview cost evaluation input

4 RESULTS

The literature search resulted in eighteen conversion routes from cresol to other compounds. Those conversion routes are graphically presented in Figure 4.1 and more in detail in Table A.1 in Appendix A. A first step that is in multiple conversion routes present, is the general methylation of the hydroxy-group to a methoxy group with the compound $(CH_3)_2SO_4$. This methoxyphenol functions as an intermediate for some of the conversion routes. Some of these products have interesting applications, for example musk ambrette is widely used as a fragrance but also has toxicological properties. Therefore, the use of this chemical is declining in developed countries [66]. The other products and conversion routes are evaluated in the same manner. After this first selection based on the application, seven products (and conversion routes) were still considered to be interesting for cresol conversion: toluene / BTX (4), p-hydroxybenzaldehyde (7), butylated hydroxy toluene (8), vanillin (9), TMBA (10), ECN resins (17) and BCNTs (18).
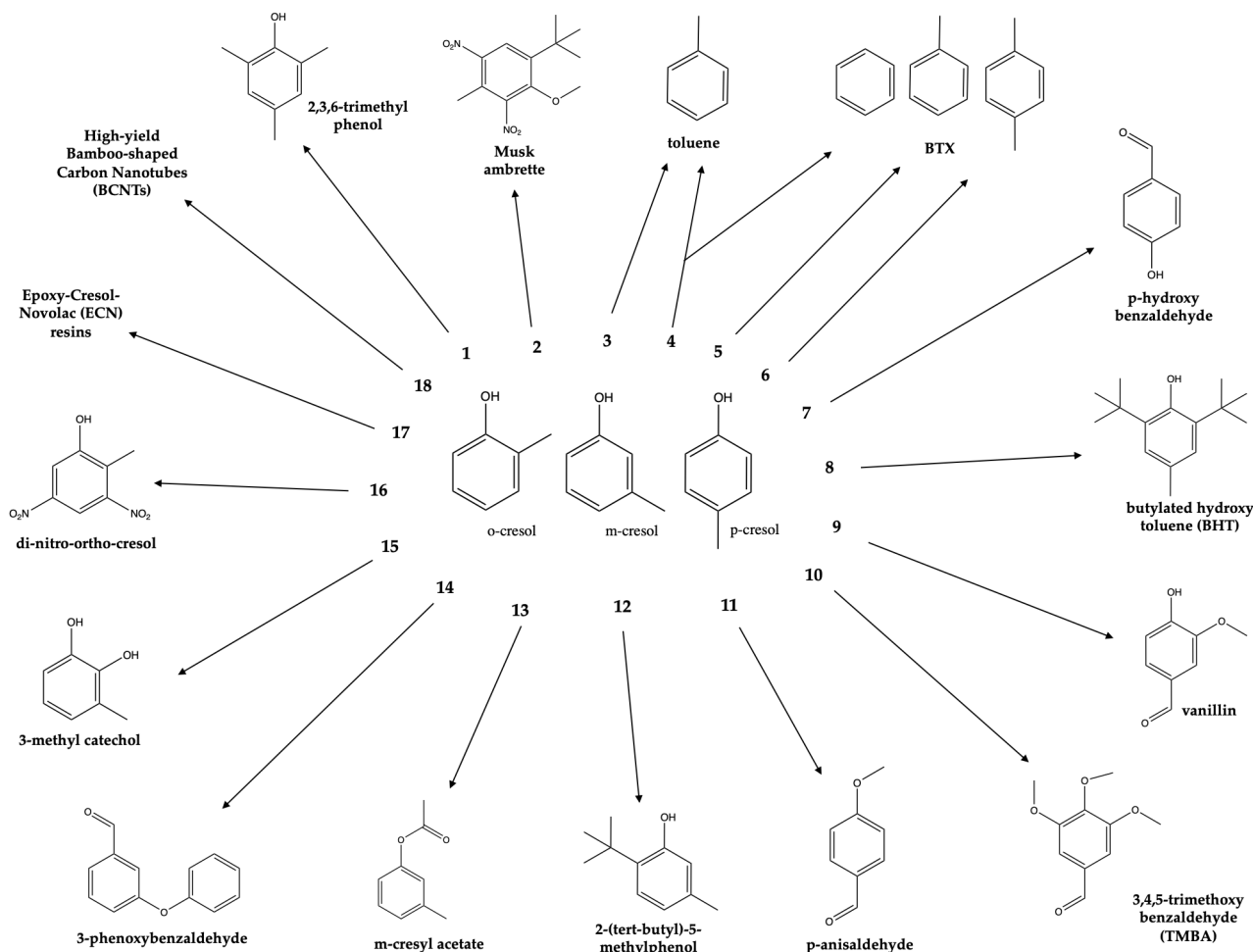
Figure 4.1: Overview of the cresol conversion routes (o-ortho; m-meta; p-para)

BTX are the compounds Benzene, Toluene and Xylene. One of the primary methods of producing BTX is in petroleum refineries. In those refineries, naphtha is catalytic reformed to recover different aromatics. This process emits a large amount of CO_2 and is dependent on fossil sources. The application of BTX has a wide range, from advanced plastics to chemicals to a fuel source [4]. The interesting thing about this selected conversion route is that since the cresol is based on biomass, this BTX will be bio-based. P-hydroxybenzaldehyde is used in a lot of different industries. It is mostly used as an intermediate or raw material in the pharmaceutical and food industry. An example for the pharmaceutical industry is that it serves as a key raw material in the production of a certain penicillin type. Besides this, it is also used in perfumes and pesticides. [67] BHT is mainly used as antioxidant, but there is still quite a debate whether or not the compound is entirely safe. An example for replacing BHT is for example vitamin E [68], [69]. The compound vanillin is widely known with as main application the food industry. The amount of vanillin used in the food industry is in-creasing over the years and will increase more the following decade [70]. TMBA (3,4,5-trimethoxy benzaldehyde) is widely used as intermediate for an antibiotic, but the expectations are that the product demand market will not grow anymore the next decade [66]. The ECN (Epoxy-Cresol Novolac) resins (17) are used more and more in the electronic industry for various applications, meaning that the market for those resins is expected to grow [66]. The Bamboo-shaped Carbon Nanotubes (BCNTs, 18) have electrochemical characteristics and can provide high electron transfer rates, which are important for innovative applications [71].

Compared with the possible cresol conversion possibilities, the amount of conversion routes that are based on the specific compound creosol are much less. The routes are visible in Figure 4.2 and the routes are in more detail noted in Table A.2 in Appendix A. Most of the synthesized compounds were made with the goal to try a specific reagent or reaction type, such as ozonolysis or reactions with radicals. Those reactions did not result in a product with an application.
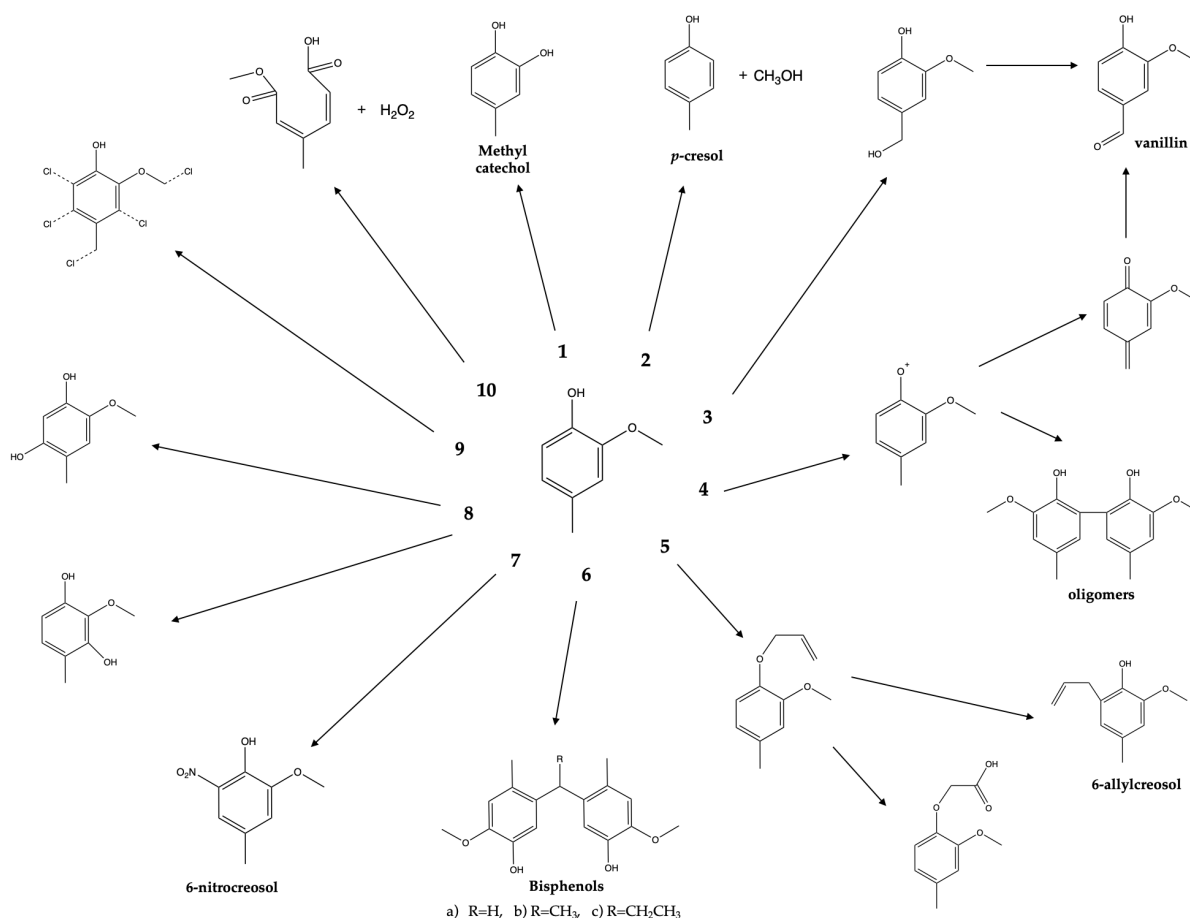
Figure 4.2: Overview of the creosol conversion routes

The products (and conversion routes) that were of interested in regard to the applications are: 4-methyl catechol (1), vanillin (3,4) and the bisphenols (6). For example, 4-methyl catechol can be used as an antioxidant [72]. The importance and applications of vanillin are widely known. The renewable bisphenols obtained from creosol conversion have the possibility to replace bisphenol A in a sustainable way.

There also is a conversion route from creosol to p-cresol via a hydrodeoxygenation reaction [73]. This implicates that all the conversion routes of cresol can also be done with creosol if the hydrodeoxygenation reaction is first performed.

After this selection, there were still nine interesting compounds left. Therefore the explained Green Chemistry rating method is applied. One example will be discussed in more detail to demonstrate this method and the achieved results by this method. This is done for butylated hydroxy toluene (BHT) and is shown in Table B.1 in Appendix B. The other compounds are all graded in the same manner. An overview the average grades is given in Table 4.1 and the entire grading table in Appendix C.

Product	Average
p-hydroxy benzaldehyde	
• catalytic	3.7
• enzymatic	3.6
Vanillin	
• catalytic	2.9
• enzymatic	3.4
Bisphenols	3.2
Methyl catechol	3.0
BHT	2.2
TMBA	2.3
Carbon Nanotubes	2.6
Epoxy-Cresol-Novolac Resins	3.2
BTX	
• Toluene	3.3
• Benzene	3.1
• Xylene	3.1

Table 4.1: Ranking of the conversion routes

This resulted in the best green chemistry scores for the compounds p-hydroxybenzaldehyde, enzymatic vanillin, bisphenols, ECN resins and toluene / BTX. The three products with the highest score were: p-hydroxybenzaldehyde (catalytic route), toluene / BTX and ECN resins. Since it is also interesting to compare a chemical, a possible fuel and a resin with each other

in terms of the process, those three conversion routes were chosen to do a process design of. One major reason for selecting p-hydroxybenzaldehyde is the more innovative and green reaction than the conventionally used methods. The two industrial ways of preparing p-hydroxybenzaldehyde are from phenol or p-nitrotoluene. The phenol route consists of multiple reaction steps. Advantages of this conversion route is the readily available raw material and the simple production process. However, the yields are low and the costs are high. The process with p-nitrotoluene as starting material has as advantage that the price of p-nitrotoluene is low. The disadvantages are however the process requires a number of process steps and equipment. The reaction conditions are requiring a high energy consumption and a toxic intermediate is formed. These industrial routes use toxic compounds like formaldehyde, chloroform and chromic acid and therefore, the production of p-hydroxybenzaldehyde from cresol is a good and green alternative. [67], [74] The main reason for selecting BTX is the fact that the demand for BTX will continue to grow, whereas the use fossil resources is expected to decrease. Therefore other possibilities for obtaining BTX are necessary. [4]

4.1 P-HYDROXYBENZALDEHYDE

The applications of p-hydroxybenzaldehyde were already mentioned, it is used in a lot of different industries either as intermediate compound or product, amongst others in the pharmaceutical and the food industry. There are multiple conversion routes possible for the conversion of cresol to p-hydroxybenzaldehyde (HBA). Already mentioned are the enzymatic [75] and one synthetic way [76].

Based on the article of Wang et al. [76], a block diagram was drawn, as shown in Figure 4.3. A more extensive block diagram with the reaction conditions is shown in Appendix D.1. The patent issued by Rohrscheid [77] gives a method for the further isolation of HBA which corresponds greatly with Wang et al. and is more detailed.

The first block represents the catalytic oxidation reaction (75°C, 0.3 MPa) from p-cresol (99% conversion) with molecular oxygen to HBA as main product according to reaction 4.1.

$$C_7H_8O + O_2 \rightarrow C_7H_6O_2 + H_2O \qquad (4.1)$$
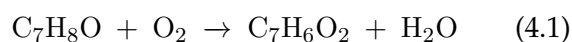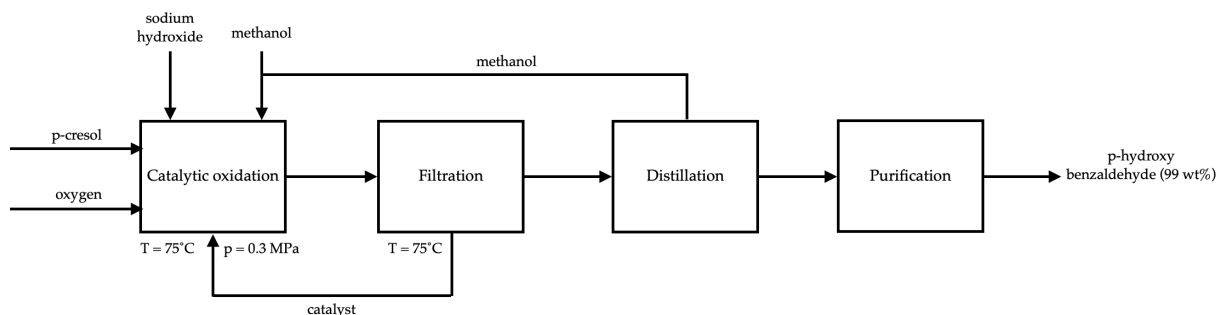
Figure 4.3: Block diagram of p-hydroxybenzaldehyde production

This reaction has a selectivity of 96%, indicating that there is also a side reaction. In this case, this is the continued oxidation of the p-hydroxybenzaldehyde to p-hydroxybenzoic acid with a selectivity of 4%:

$$2\,C_7H_6O_2 \,+\, O_2 \,\rightarrow\, 2\,C_7H_6O_3 \qquad (4.2)$$
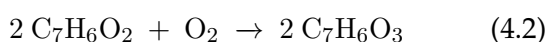
The catalyst that was researched to have the highest selectivity to HBA, was the Copper-Manganese (CuMn; Cu: 7.4 wt%, Mn: 1.4 wt%) bimetallic catalyst on active carbon support. Besides this catalyst, sodium hydroxide is also added with a catalytic function to increase both the selectivity and activity. The whole reaction is done with methanol as solvent, which decreases the reaction time compared with water as solvent. The complete reaction mixture with the components is thus a three phase system. Therefore, there is a possibility that mass transfer might be the rate determining step for this reaction. The products of this first reaction step are not in the form of p-hydroxybenzaldehyde and p-hydroxybenzoic acid, but as the alkali metal salt.

The remaining components in the product stream have to be separated to obtain HBA in a desired purity. First, the catalyst is separated by filtration (or centrifugation) from the reaction mixture at 75°C. The solid fraction contains both remaining catalyst solid particles and precipitated cobalt oxide-hydrate. The catalyst solid particles can be completely recovered and recycled back to the catalytic oxidation reactor by first washing with methanol, then drying at 120°C and a calcination reaction at 400°C. The vapour/liquid mixture enters a distillation column in which the methanol is separated from the other components. The remaining liquid is cooled to about 0-5°C, causing the sodium salt of HBA to crystallise out, supposedly in the form of leaflets. The crystals are suction-drained and washed with a sodium hydroxide solution. Water

is added to dissolve the HBA sodium salt, after which the mixture is heated to 60°C. Hydrochloric acid is added to the sodium salt, causing HBA to precipitate. The solid HBA product is filtered, washed with water and dried at 40°C. [77]

The theoretical process was modelled in Aspen Plus™. Besides HBA, the side product p-hydroxybenzoic acid is also formed. However, there are no defined properties in Aspen Plus™ for this compound. One of the isomers of this chemical, namely 2-hydroxybenzoic acid or also called salicylic acid, does have defined parameters. The two isomers have quite similar characteristics like the melting point range, the boiling point and density [78], [79]. Therefore, the assumption is made that salicylic acid can replace p-hydroxybenzoic acid in the model.

The catalysts sodium hydroxide and CuMn are not reacting in this process and are therefore not taken into account. However, officially it is the case that sodium hydroxide participates in the reaction by creating a sodium salt, which will become p-hydroxybenzaldehyde after the acidification with hydrochloric acid. It is assumed that the sodium salt formation and the acidification are occurring in such a way that all the sodium hydroxide and hydrochloric coming in the system are equal to the amounts going out of the system. This is assumed to happen all in one reactor block. The optimisation steps resulted in an optimal purge to recycle ratio of 1 to 9.

Changing the pressure and temperature of the crystallisation, centrifuge and distillation did not have any significant effects. Those assumptions led to the simulation overview and results obtained as shown in Appendix D.2 and D.3. The final product p-hydroxybenzaldehyde is obtained as a solid in a 99.98 wt% purity.

Subsequently, a cost analysis was made based on the obtained data. The entire cost analysis is

shown in Appendix D.4. The result is a gross profit of $-1.28 million per year, see Table 4.2.

	$MM/year	$/kg product
Variable Cost of Prod.	0.03	646.29
Fixed Cost of Prod.	1.26	32,442.41
Cash Cost of Prod.	1.29	33,088.70
Pyrolysis Costs	9.44 E-5	2.43
Gross Profit	-1.28	-33,041.13
Total Cost of Prod.	2.23	57,350.81

Table 4.2: Overview of the cost analysis for a production capacity of 38.8 kg/yr

The manufacturing costs are calculated by adding the raw material, consumables, waste, utilities, fixed operating and investment costs [80]. This resulted in a manufacturing cost of $57 million per ton p-hydroxybenzaldehyde.

At a production scale of 50 ton p-hydroxybenzaldehyde per year, the plant was profitable. The entire market of p-hydroxybenzaldehyde is not exactly known, but is estimated to be around 500 ton/yr only in the USA and is expected to grow more over the following years [81]. Therefore, a capacity of 50 ton/yr seemed like a reasonable choice.

A comparison of the reactant inputs is shown in Table 4.3, the reactant flows which are not added in the Aspen Plus^{TM} simulation environment are also given in order to provide a complete overview. For the overview, Aspen Plus^{TM} was abbreviated to just Aspen.

	Lab	Industry	Remarks
pine	0.066	76.29	Not in Aspen
cresol	0.0054	6.96	
oxygen	0.0019	2.47	Assumption
MeOH	0.014	17.38	With recycle
NaOH	0.0015	1.97	Not in Aspen
HCl	0.0033	4.22	Not in Aspen
CuMn			Not in Aspen
Cu	8.0E-7	8.24	
Mn	2.0E-7	2.06	

Table 4.3: Overview of the reaction input (kg/hr)

Based on this industrial scale, another cost estimation was performed. It should be stated that the fixed capital investment is quite the same compared with the lab scale, because of the previously mentioned reason that the industrial equipment was too large for the lab scale but was restricted to minimal sizes and capacities. This

resulted in Table 4.4 and a complete overview of the cost estimation in Appendix D.4. The payback time was calculated to be 6.9 years.

	$MM/yr	$/kg product
Variable Cost of Prod.	0.004	0.08
Fixed Cost of Prod.	1.32	26.35
Cash Cost of Prod.	1.32	26.43
Pyrolysis Costs	0.11	2.19
Gross Profit	1.07	21.39
Total Cost of Prod.	2.70	54.03

Table 4.4: Overview of the cost analysis for a production capacity of 50 ton/yr

The manufacturing costs were calculated to be $57,020.00 per ton p-hydroxybenzaldehyde.

4.2 BTX / TOLUENE

The theoretical design of the BTX product was mainly based on the article of Liu et al. [82]. In this article, they are able to obtain roughly 100% selectivity towards toluene with a NiFe catalyst. Another reason for choosing this article as main reference is the fact that they describe both the kinetics and the thermodynamics by theoretical models and experimental data.

There are officially many reactions occurring, also with the formation of radical intermediate products. However, the vast majority of those reactions do not result in a significant amount of reaction products, only trace amounts. The main reason for this is that most of the reversible kinetic constants of those reactions (k^-) are factors ten or more higher than the forward reaction rates [82]. This results in three dominant reactions when the process is performed at 200°C with the NiFe catalyst. This statement was proven both by kinetic data as experimental data according to Liu et al. [82]. The first reaction is known as the direct dehydroxylation of m-cresol to toluene according to equation 4.3.

$$C_7H_8O + H_2 \xrightarrow{k^+=1.9} C_7H_8 + H_2O \quad (4.3)$$
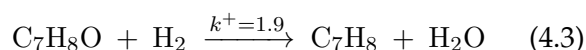
However, this is not the most dominant reaction. The mixture of cresol with hydrogen can also react to 3-methylcyclohexa-2,4-dien-1-ol ($C_7H_{10}O$), shown in equation 4.4 [82].

$$C_7H_8O + H_2 \xrightarrow{k^+=70} C_7H_{10}O \quad (4.4)$$
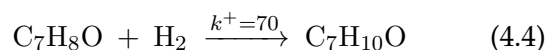
According to the forward kinetic constants (in s^{-1} of the two equations, it can be already clear that equation 4.4 is kinetically favorable. Both equations are however also reversible, with those kinetic constant respectively being 6.2×10^6 and $0.074\ s^{-1}$. This also indicates that the reversible reaction of the dehydroxylation proceeds quickly.

The product of equation 4.4 will quickly react again to toluene and water by the cleavage of the C–O bond according to equation 4.5.

$$C_7H_{10}O \xrightarrow{k^+=150,000} C_7H_8 + H_2O \qquad (4.5)$$
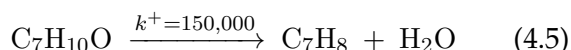
As previously mentioned, those reactions proceed as described when the reaction is performed at 200°C with the NiFe catalyst. This catalyst is loaded in a fixed bed reactor with a pressure of 1 atm. Before the reactants enter the fixed bed reactor, they are mixed and vaporized in a vaporizer at 190°C. The hydrogen/feed molar ratio was in the range of 70-80 to 1. This ensured that the catalyst deactivation was minimized, and the kinetic rates were thus ensured to be correct. After the reaction in the fixed bed reactor, the reaction mixture contains hydrogen gas, water and toluene. The hydrogen gas can be separated and recycled by using a pressure vessel which decreases the pressure and temperature to make the separation optimal. Henry's law states that the solubility of a gas in a liquid is proportionally to the pressure of a gas, meaning that decreasing the pressure will decrease the solubility of the gas in the liquid phase. Since the goal is the best separation of the two phases as possible, decreasing the pressure seems like a valid option. At the same time, the temperature is lowered in order to decrease the solubility even more. [83]

The remaining hydrogen gas can be recycled to the hydrogen feed stream. The liquid phase continues to a decanter in which the aqueous and organic phase (toluene) are separated. The block diagram of the process is shown in Figure 4.4.

The theoretical design was modelled with the Aspen Plus$^{\text{TM}}$ simulation environment. Since the kinetics of the reaction were known, a plug flow reactor model was chosen. The activation energies and kinetic constants of the corresponding chemical reactions are given in Appendix E.1. As with the side product from the p-hydroxybenzaldehyde process, the 3-methylcyclohexa-2,4-dien-1-ol ($C_7H_{10}O$) did not have any parameters in Aspen Plus$^{\text{TM}}$. This product is however mainly an intermediate compound in the reaction to form toluene again. Therefore, a kind of similar compound was chosen: 3-methylcyclohexanol (MCOL, $C_7H_{14}O$). The main difference seems to be the amount of hydrogen used in the reaction from cresol to MCOL, as visible in equation 4.6. From the referenced article, it is not entirely certain on what the kinetics of the reaction depend, if they depend on the molarity or concentration of hydrogen, this assumption is very approximate.

$$C_7H_8O + 3\,H_2 \rightarrow C_7H_{14}O \qquad (4.6)$$
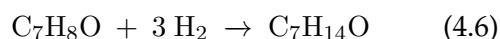
However, when MCOL reacts to toluene it also releases hydrogen gas, which can be seen in equation 4.7.

$$C_7H_{14}O \rightarrow C_7H_8 + H_2O + 2\,H_2 \qquad (4.7)$$
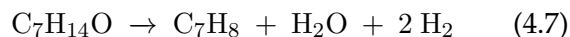
Therefore, the overall reaction with MCOL as intermediate can be shown according to equation 4.8. This is completely similar to the overall equation of the reactions to the official intermediate and therefore the assumption is made that those reactions can be used to simulate the process.

$$C_7H_8O + H_2 \rightarrow C_7H_8 + H_2O \qquad (4.8)$$
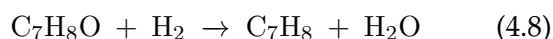
The hydrogen pressure was kept high, with a H_2/feed molar ratio of 70 to 1. 90% of the hydrogen stream coming out of the gas/liquid separator could be recycled back to the inlet stream of hydrogen and 10% was purged.

Figure 4.4: Block diagram of BTX production

The reaction via the intermediate MCOL and subsequently to toluene, is a reaction in series. Two plug flow reactors were modelled since Aspen Plus^{TM} was not able to perform the reactions in one reactor. The result is a 100% selectivity to toluene with a final purity of 99.85 wt%.

After this technological assessment at small scale, an economic analysis was performed. Since this report is all about green chemistry and sustainability, a note should be made about the used hydrogen price. There are multiple types of hydrogen, from non-sustainable to sustainable: grey, blue and green. The hydrogen costs of these three types also differ from respectively \$1.00-1.80/kg, \$1.40-2.40/kg to \$2.50-6.80/kg [84]. At the moment, green hydrogen is just in pilot scales processes. Therefore the choice is made to use blue hydrogen, since the pilot scale supply is not yet enough to be able to supply this process and other customers. The use of blue hydrogen makes sure that the carbon emissions are captured, stored or reused [85]. For industrial bulk amounts, prices are expected to be not as high as the ones just mentioned, so the lower limit of blue hydrogen price (\$1.40/kg) was used.

The company BioBTX was contacted and provided some information about the prices of BTX and the separate compounds. When oil prices are \$60 per barrel, the prices of toluene, benzene and p-xylene are roughly \$800/ton, \$900/ton and \$1050/ton respectively. For those types of products, there is not really a premium for green products. A good assumption was that the price will increase about 10-20% when BTX is green. At the moment, the oil prices are lower due to circumstances, but the just mentioned data is taken and thus the assumption was made that the oil price is generally \$60 per barrel (about 159 liters).

An overview of the cost analysis is shown in Table 4.5 and more in detail in Appendix E.4.

	$MM/ year	$/kg product
Variable Cost of Prod.	0.13	37.56
Fixed Cost of Prod.	1.22	358.02
Cash Cost of Prod.	1.34	395.58
Pyrolysis Costs	0.01	2.57
Gross Profit	-1.35	-397.35
Total Cost of Prod.	2.13	625.84

Table 4.5: Overview of the cost analysis for a production capacity of 3.4 ton/yr

The result is a loss of \$1.35 million per year.

The manufacturing costs were calculated to be \$623,270.00 per ton.

Subsequently, the process capacity is increased. A capacity of 10 kton/year was chosen since the total market of toluene is estimated to be around 34 million ton/year in 2023 [86]. The BASF plant in Ludwigshafen produces 300 kton/year [87]. However, about 83% of that is used for the production of benzene, which is not the desired market of this product, since the goal is to replace high-value chemicals. Therefore a capacity 10 kton/year seems reasonable.

	Small	Industry	Remarks
pine	5.315	17,956	Not in Aspen
cresol	0.5	1,471	
H_2	0.082	214.2	
NiFe		0.025	Not in Aspen
Ni	0.00025	0.025	
Fe	0.00025	0.025	

Table 4.6: Overview of the reaction input (kg/hr)

Based on this new production capacity of 10 kton/year, a cost estimation was made. An overview of the results is shown in Table 4.7. The manufacturing costs were \$2,318.00 per ton.

	$MM/ year	$/kg product
Variable Cost of Prod.	18.07	1.81
Fixed Cost of Prod.	1.79	0.18
Cash Cost of Prod.	19.87	1.99
Pyrolysis Costs	25.72	2.57
Gross Profit	-37.59	-3.76
Total Cost of Prod.	48.87	4.89

Table 4.7: Overview of the cost analysis for a production capacity of 10 kton/year

When the prices of BTX are assumed to be 20% higher than normal BTX prices because both the feedstock and the production method is green, the maximum price is \$960/ton. The only thing that will change is the Gross Profit. This will have a new value of \$-35.99 MM per year and \$-3.60 per kg toluene (Figure E.8, Appendix E.4). The process was profitable with a toluene price of \$4.50/kg (Figure E.9, Appendix E.4).

4.3 ECN RESINS

The third chosen interesting compounds were the Epoxy-Cresol-Novolac resins. The applications are mainly in electronics and the application range of these resins is expected to grow [66].
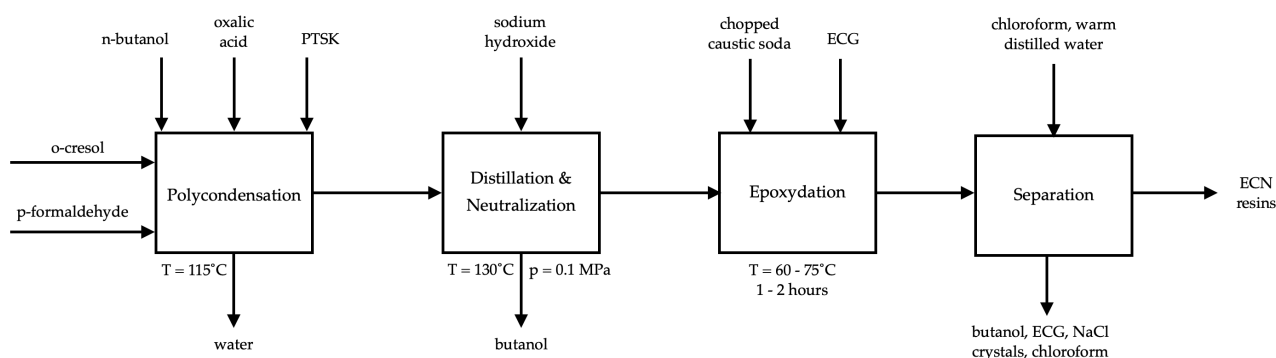
Figure 4.5: Block diagram of ECN resin production

The reaction of ortho-cresol to the resins occurs in a two step process. A polycondensation reaction of cresol with p-formaldehyde will yield Cresol-Novolac resins. An additional reaction with epichlorohydrin gives the desired Epoxy-Cresol-Novolac resins. [88] A block diagram is drawn in Figure 4.5 based on the cited references and more extensively in Appendix F.
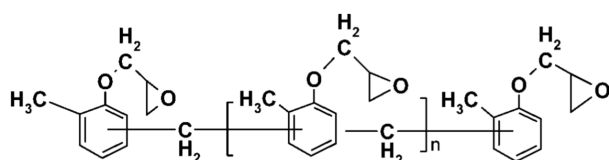
Figure 4.6: ECN resin

Although data on conversion and yields are reported in literature, this process is still much in development. The only found conversion route was a Russian Patent [88], which made it hard to extract useful data and to evaluate the reliability of the data and patent. Therefore the decision was made to focus on the other two conversion routes, HBA and BTX/toluene.

5 DISCUSSION

Two processes were evaluated via both the technological and economical aspects after selecting conversion routes from cresol to product, based on the green chemistry principles. In order to define if a process is technologically feasible, some parameters are set according to Krishna [89]. The process should operate with feasible temperature, pressure and residence time values. The operation should be intrinsically safe, without any instabilities. A maximum possible conversion of the feedstocks and a maximum selectivity of the reaction to the desired products should be achieved. The process should operate in the most sustainable way as possible. The economic

feasibility is mostly based on evaluating the costs of the raw materials, the amount and therefore price of equipment pieces and the total cost of production and gross profit of the process. Additionally, in order to see if these processes could have potential to replace conversion routes based on other starting materials, they should be compared.

An important assumption that was made during the process design of all three compounds, was that the industry scale yields were taken to be the same as the lab scale yields. The process steps that were taken in the lab scale experimental set-up were transformed to industrial scale. Currently there is no data available for this scale-up of laboratory yields to industrial scale, so further research should prove if this assumption is valid.

According to the set parameters, the process of p-hydroxybenzaldehyde seems technologically viable. The temperatures were generally below 100°C, however the pressure was increased for the reaction. The pieces of equipment were considered to be safe. A feedstock conversion of 99% and a selectivity of 96%, optimised by selecting a good catalyst, were considered to be high. The methanol could be recycled for 90% and the catalysts also had the potential to be recovered and recycled entirely. It should be stated that the actual recycle stream of methanol could be higher in reality, but due to accumulation problems with Aspen Plus™, this value was chosen. The selectivity of the reaction was high and resulted in a purity of 99.98 wt%. Besides the catalysts, methanol and p-cresol, only hydrochloric acid and molecular oxygen were used.

As expected, the lab scale of the production of p-hydroxybenzaldehyde was not feasible. However, the process with the industrial produc-

tion capacity for p-hydroxybenzaldehyde was profitable. According to Agam [81], the sales turnover in the USA with a production capacity of 500 ton/yr was 10 million US Dollars. This is thus corresponding to about 1 million US Dollars profit per 50 ton/yr production. For this designed plant, the production scale of 50 ton/yr was chosen, which resulted in a gross profit per year of $1,069,423.97$. Although the cost estimation is a really approximate one, the plant seems to be able to make quite some profit. Compared with the just mentioned sales turnover in the US with the same production capacity, the plant seems to be equally profitable. Also, the price of p-hydroxybenzaldehyde used, was based on normal industrial prices ($50 per kg). It is not known if there is a certain premium price for p-hydroxybenzaldehyde when it is bio-based.

The two main industrial preparation methods for p-hydroxybenzaldehyde were explained and considered to be undesired due to the toxicity of the compounds. The described process from cresol has is advantages, like low raw material costs, high selectivity, good recyclability of the solvent and a relatively short process due to the one step reaction. The main disadvantages are however that the costs of production are high due to the pyrolysis process on forehand and therefore also equipment needs to be purchased. However, it should be stated that the other pyrolysis products with a certain value are not taken into account. Still, these costs increase the risk significantly when investing in this process. The variable costs of production are low ($0.08) compared with the fixed cost of production ($26.35) per kilogram product. When compared with the lab scale, the fixed costs did not change a lot when scaling the process up. This is due to the assumption that industrial equipment has a minimal size, causing the lab scale to have too big equipment volumes compared to the necessary minimal reaction volume. When Tables 4.2 and 4.4 are compared, it is visible that the variable cost of production in million dollars per year is less when increasing the production capacity. This seems not correct due to the fact that the costs of the raw materials increase a lot. However the reason for this is that the byproducts of these processes were taken into account for extra profit and were subtracted from the variable costs. Since the industrial scale produces besides the HBA also a lot of 4-hydroxybenzoic acid, the money that could be made by selling this will

decrease the variable costs. It should be stated that the assumption was made that this byproduct can be retrieved quite easily from the waste stream, which is supported by the fact that it is soluble in ether and alcohols and less soluble in water [90]. Therefore, a relatively simple extraction and subsequently distillation of the solvent can be performed to purify the byproduct.

Since the fixed costs increased more than the variable costs, it could be implied that when the production capacity is scaled up even more, more profit can be made. However it should be taken into account that the market size for p-hydroxybenzaldehyde stays the same in a short period of time. A general and well-known economic principle states that when increasing the supply with a constant demand, the price will decrease.

The hypothesis for the BTX/toluene process was that it is technologically feasible, but economically not. In order to evaluate the technological feasibility, the same parameters as mentioned for p-hydroxybenzaldehyde are used, according to Krishna [89]. The BTX/toluene process only used hydrogen as reagent besides the cresol. The amount of hydrogen was supplied in a 70 times higher molar ratio than cresol, but 90% of the unreacted hydrogen gas could be recycled according to Aspen Plus[TM]. It is possible that in reality more hydrogen can be recycled, but due to accumulation in the recycle stream model, this can not be proven. The reaction was operated at high temperatures (around 200°C) and at normal atmospheric pressure. Hydrodeoxygenation reactions are typically exothermic [91], so in terms of safety it is important to make sure the reactor is cooled in a safe and totally controlled manner.

The results of the BTX modelling showed a 100% selectivity towards toluene with only trace amounts of intermediate product. It can be assumed that this is quite realistic and acceptable, but it should be taken into account that this selectivity might become less when operating at industrial scale. This complete selectivity towards toluene also means that the assumption that was made about the reactions with a different intermediate compound was proven to be correct, since only trace amounts of this intermediate compound are present which will not affect anything in either the product or the process.

All things considered, it can be stated that the process is technologically feasible, also compared

with other production methods of BTX which typically use petrochemical sources. The advantages of this process from cresol are the complete selectivity towards toluene and the recyclability of the unreacted hydrogen. The disadvantage is a high operating temperature in combination with an exothermic reaction.

It should be stated that in this case, only toluene is produced and not the other components of a standard BTX mixture: benzene and xylene. Therefore, instead of using this obtained toluene as a fuel, like BTX, it can also have the application of green solvent. However, it is important to realise that the obtained cresol from pyrolysis liquids is not highly pure, as was the assumption for the modelling later on. More research has to be performed in order to know the exact selectivity and reactions from not highly pure cresol obtained from biomass with this specific catalyst and reaction conditions.

If Tables 4.5 and 4.7 are compared, the first thing to notice is that both scales have a quite high profit loss and that the industrial scale might even be less profitable than the smaller scale. However, when the gross profit per unit (kg) product is studied, it is actually the case that the industrial scale ($-3.76) turns less loss than the smaller scale ($-399.61) per unit product.

The reason for this is the increase in the variable cost of production due to the costs of the raw materials. Those variable costs are quite enormous compared with the increase in the fixed cost of production. The main reason for the quite enormous profit loss is the low value of the toluene. Due to this low value, the costs of the raw materials (per kg toluene) are four times higher than the price of toluene. When more product is desired, the amount of raw materials has to increase, causing a rapid increase of the costs of these raw materials. The costs per unit are however lower when scaling the process up due to the fact that simply more product is made so the costs are divided over more product units. When increasing the production scale, a larger amount of pine wood needs to undergo the pyrolysis process. This doubles the costs per unit product. As mentioned before, the other pyrolysis products are not taken into consideration and will probably decrease the loss due to their value.

The company BioBTX mentioned that the price of BTX may be increased by about 10 to 20% when producing it in a green manner. So, using this new price, the cost estimation was performed again. However, compared with the values of the Gross Profit in Table 4.7, there is not a huge difference. The raw material and the pyrolysis process costs per product unit are still higher than the proceeds per product unit. Besides this, the toluene price was calculated when the desired result was a positive gross profit, with as result $4.60 per kilogram toluene. This is way above the normal prices of toluene and bio-based toluene. Therefore, this production method is not viable for toluene production.

When this process towards BTX is considered, it should be taken into account that the assumption was that first cresol was produced. However, with regards to these obtained results, it might be more viable to produce BTX directly from pyrolysis liquid instead of first performing the difficult separation steps to obtain cresol in its pure form. A disadvantage for this might be that in this case, toluene is obtained in a high purity with 100% selectivity. This pure toluene can be used as solvent in the chemical industry. However, if the goal is to replace non-sustainable fuels with bio-based BTX fuels, a production route directly from pyrolysis liquid might be favourable, both technologically and economically [92].

Overall, multiple things were assumed and some shortcuts were taken in order to be able to perform this research in a relatively short time frame. It was not mentioned yet that the separation costs to fractionate the pyrolysis products to cresol and creosol were not taken into consideration. However, the other valuable products besides these two compounds were also not accounted for in the cost estimation by adding extra profit.

As for the model in Aspen Plus^{TM}, it should be stated that this was based on quite some assumptions and shortcuts as well. One example that is highlighted is the use of the DSTWU distillation column instead of for example a more extended RadFrac column. It was assumed that the DSTWU's were good enough due to the fact that the results from these simulations were corresponding with the results from the articles used as references. It was also already mentioned that the purge to recycle stream ratio's can be improved in reality, but that the model was not able to prevent the accumulation when this improvement was done.

5.1 FUTURE PERSPECTIVE

In order to increase the share of bio-based compounds in the chemical industry, more research should be performed about the most technologically and economically feasible routes based on the pyrolysis of biomass. Specifically on the effects of the biomass pyrolysis product in terms of purity towards the conversion routes that are already known.

Based on this study, more research should be performed about the influence of cresol from pyrolysis liquids on this specific reactions, as well as the influence of using a combination of the three isomers instead of a pure isomer.

Further research can also be performed with the Epoxy-Cresol-Novolac resins, which are considered to have innovative applications and an increasing demand.

6 CONCLUSION

The goal of this research was to provide a process design of interesting conversion routes from the products of the pyrolysis of biomass towards other chemicals. A background study was performed to find the optimal conditions for the starting materials of the process design: cresol and creosol. The result of this was the fast pyrolysis of pine wood sawdust which resulted in the highest yield of the phenolic fraction and thus high amounts of cresol and creosol. Subsequently, conversion routes from those two compounds were researched and based on the green chemistry principles the choice was made to design a process of cresol to p-hydroxybenzaldehyde and BTX/toluene.

Based on the evaluation of the results, it can be concluded that the conversion of cresol to p-hydroxybenzaldehyde via catalytic oxidation is both technologically and economically feasible. It is however important to state that the effects of using not entirely pure cresol and a mix of the three isomers are not known for this specific process. In order to provide a complete recommendation for the pyrolysis of biomass to produce pyrolysis liquids and subsequently perform the reaction towards p-hydroxybenzaldehyde, those effects need to be studied in detail. It can however be concluded that the pyrolysis of biomass and the subsequently obtained products, definitely have interesting properties for conversion towards chemicals with high interest and possibly value.

The conversion route of cresol to BTX/toluene has advantages that other commercial routes of producing BTX/toluene do not have. The most important advantage is the fact that this route from biomass and cresol as intermediate is completely bio-based, whereas at the moment BTX and toluene are still predominantly produced from petrochemical sources. The reason for this is however the more unfortunate part of this research: the costs of production. The BTX/toluene production from cresol is not economically viable, as expected. The production from petrochemical sources is much cheaper. However, as mentioned in the discussion, the process does has it advantages, but a direct conversion route of pyrolysis liquids towards BTX might be more feasible.

7 ACKNOWLEDGEMENTS

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A Tables

		Product	Reaction	Other reagents	Catalyst	Reference
1	Meta	2,3,6-trimethyl phenol	Methylation	Methanol		[66]
2	Meta	Musk ambrette	Methylation, butylation, nitration			[66]
3	Meta	Toluene	Hydrodeoxygenation		Pt	[93]
4	Meta	Toluene / BTX	Dehydroxylation	H_2	Fe or NiFe	[82], [94]
5	Meta	BTX	Hydrodeoxygenation and methyl transfer	H_2	Pt / HBeta	[93]
6	Para	BTX	Hydrodeoxygenation	H_2	Ni_2P/SiO_2-3	[95]
7a	Para	p-hydroxy benzaldehyde	Electrochemical oxidation	Ferroceneboronic acid		[75]
7b	Para	p-hydroxy benzaldehyde	Enzymatic oxidation			[75]
7c	Para	p-hydroxy benzaldehyde	Catalytic oxidation	O_2, methanol	CuMn	[74], [76], [77]
8	Para	Butylated Hydroxy Toluene (BHT)	Alklylation, dealkylation	Isobutylene, isopropyl alcohol	Sulfuric acid	[66]
9	Para	Vanillin	Bromination, methoxylation, oxidation			[66]
10	Para	3,4,5-trimethoxy benzaldehyde (TMBA)	Oxidation			[66]
11	Para	p-anisaldehyde	Methylation, oxidation			[66]
12	Meta	2-(tert-butyl)-5-methylphenol	Tert-butylation	SO_3H ionic liquid		[96]
13	Meta	m-cresyl acetate		acetic anhydride		[66]
14	Meta	3-phenoxy benzaldehyde	Meta-phenoxy toluene oxidation			[66]
15	Ortho and Meta	3-methyl catechol	Enzymatic	Phenyl hydroxylase expressed by E.Coli		[97]
16	Ortho	di-nitro-ortho cresol (DNOC)	Nitration	2,4-dinitrophenol		[66]
17	Ortho	Epoxy-Cresol-Novolac (ECN) resins	Glycidylation	Formaldehyde		[66], [88]
18	All	High-yield Bamboo-shaped Carbon Nano-tubes (BCNTs)	Pyrolysis			[71]

Table A.1: Overview of the cresol conversion routes

	Product	Reaction	Other reagents	Catalyst	Reference
1	4-methyl catechol	Demethylation	HBr and heat		[98]
2	p-cresol (and methanol)	Hydrodeoxygenation	H_2	Ni_2P	[73]
3	Vanillin	Enzymatic synthesis		Vanillyl Alcohol Oxidase (enzyme)	[99]
4	Vanillin and oligomers	Oxidation	NaOH	a) $CoCl_2$, b) $CuCl_2$	[100]
5	Creosol allyl ether		Allyl bromide		[101]
	6-allylcreosol	Boiling	Allyl bromide		
	2-methoxy-4-methyl phenoxy acetic acid	Oxidation	Na_2CO_3 H_2O	$KMnO_4$	
6	Bisphenols	Brønsted acid-catalyzed coupling	HCOR	H^+	[102]
7	6-nitrocreosol	Oxidation	NO_3 radicals		[103]
8	2-methoxy-4-methyl benzene-1,3-diol		OH radicals		[104]
	4-methoxy-6-methyl benzene-1,3-diol		OH radicals		[104]
9	chlorine substituted creosol		Chlorine atoms		[105]
10	6-methoxy-4-methyl-6-oxohexa-2,4-dienoic acid	Ozonolysis	O_3 and H_2O	H^+	[106]

Table A.2: Overview of the creosol conversion routes

B BHT Green Chemistry Principles

Green Chemistry Principle	Explanation	Grade
1. Waste prevention	About 20% of the produced mass is waste	2
2. Atom economy	There is a huge amount of side products and waste	1
3. Less hazardous chemical synthesis	The process does contain a reactor with risks based on reaction conditions, but the other process steps are mainly just washing, drying and filtration	3
4. Designing safer chemicals	There is a debate about whether or not this chemical is toxic, but there are alternatives which are not toxic	1
5. Safer solvents	Isopropyl alcohol and water are used, isopropyl alcohol is not considered to be a safe solvent, but it is not used in high quantity	3
6. Design for energy efficiency	The product is distilled, dried, centrifuged and the reactor also operates at a high temperature	2
7. Use of renewable feedstocks	Isobutylene is the other reagent and typically not renewable	1
8. Reduce derivatives	The reaction consists of two steps	4
9. Catalysis	Both reaction steps are catalysed	5
10. Design for degradation	BHT is not biodegradable and possibly even toxic	1
11. Real-time analysis for pollution prevention	There is no analysis for pollution prevention at all, also not mentioned that it could be important	1
12. Inherently safer chemistry	Isobutylene and isopropyl alcohol are both highly flammable and thus not inherently safe	1

Table B.1: Green chemistry principles grading of BHT, based on [66]

C   Green Chemistry Scores (Entire table)

	BHT	1p-hydroxy benzaldehyde enzym | chem		2Vanillin enzym | chem		TMBA	Methyl catechol	Bis-phenols	Carbon Nano Tubes	ECN Resins	Benzene	3Toluene	Xylene
1. Prevention	2	4	5	4	2	2	2	5	3	3	4	4	4
2. Atom economy	1	5	5	5	3	1	4	4	3	4	4	4	4
3. Less hazardous chemical synthesis	3	4	4	4	3	2	4	3	2	2	5	5	5
4. Designing safer chemicals	1	2	2	3	3	2	3	2	3	3	2	2	2
5. Safer solvents	3	4	4	4	4	2	4	3	2	3	2	2	2
6. Design for energy efficiency	2	4	4	4	4	4	3	2	1	2	3	3	3
7. Use of renewable feedstocks4	1	4	3	2	1	1	3	1	1	1	1	1	1
8. Reduce derivatives	4	3	5	3	3	2	1	4	3	4	2	4	2
9. Catalysis	5	4	5	4	4	4	4	5	5	5	5	5	5
10. Design for degradation	1	2	2	3	3	1	2	1	1	2	1	1	1
11. Real-time analysis for pollution prevention	1	4	4	3	3	2	2	4	3	4	5	5	5
12. Inherently safer chemistry	1	4	3	3	2	2	3	3	3	5	5	5	5
Application	4	4	4	4	4	3	2	3	3	4	3	4	3
Costs5	2	2	2	2	2	4	5	5	4	3	1	1	1
Total	31	50	52	48	41	32	42	45	37	45	43	46	43
Average	2,2	3,6	3,7	3,4	2,9	2,3	3,0	3,2	2,6	3,2	3,1	3,3	3,1

1 There are two important conversion routes for p-hydroxy benzaldehyde, an enzymatic and an industrial/chemical route, both are evaluated.
2 There are multiple conversion routes for vanillin from both creosol and cresol, for this evaluation two techniques were chosen. An enzymatic route from creosol to vanillin [72] and a chemical synthesis route from p-cresol [44].
3 There are two different conversion routes known from cresol (meta and para) to toluene, both are considered because the main difference is the catalyst used.
4 The use of renewable feedstocks is in this case considered to be the feedstocks used besides the cresol/creosol (e.g. solvents, green catalysts), since otherwise this would be the same value for every compound.
5 The cost evaluation (per kg): 1 = ≤ €100,- ; 2 = ± €150,- ; 3 = ± €300,- ; 4 = ± €500,- ; 5 = ≥ €1000,-

D   HBA process design

D.1   Extended block diagram
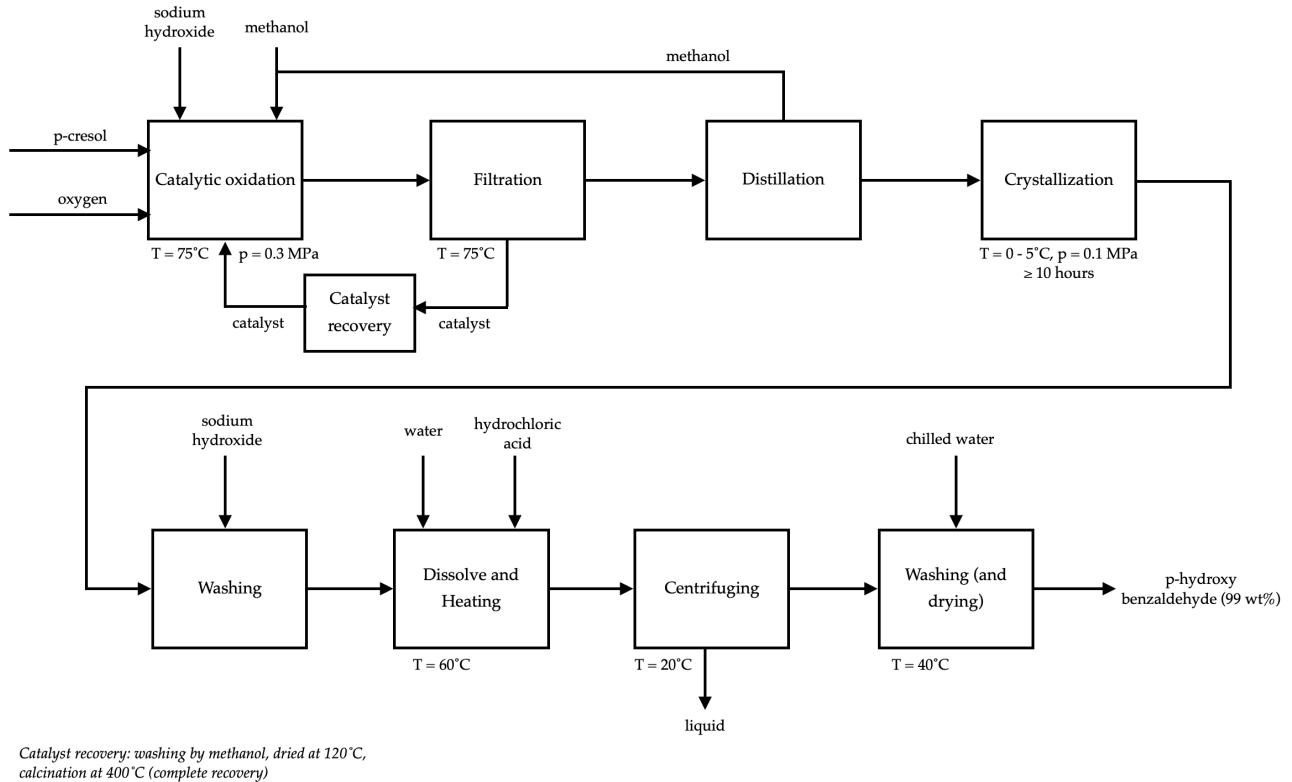
Figure D.1: Block diagram of p-hydroxybenzaldehyde production

D.2   Aspen Plus™ diagram
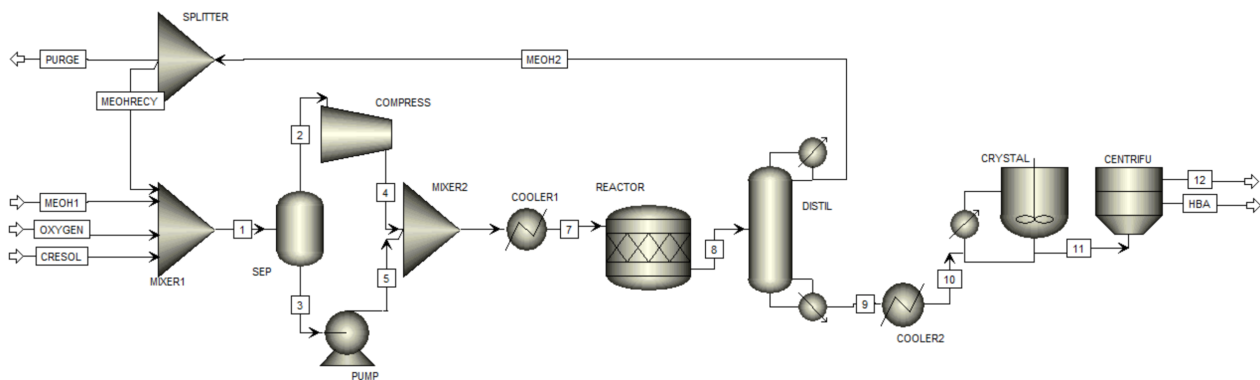
Figure D.2: Aspen Plus™ Model

D.3 Aspen Plus^{TM} input and results

```
OVERALL FLOWSHEET BALANCE
-------------------------

                  ***  MASS AND ENERGY BALANCE  ***
                        IN            OUT         GENERATION    RELATIVE DIFF.
    CONVENTIONAL COMPONENTS
          (KMOL/HR )
       O2              0.600000E-04  0.952927E-05 -0.504700E-04  0.121400E-04
       HBA             0.00000       0.733621E-05  0.475000E-04  5.47473
       P-CRESOL        0.500000E-04  0.520000E-06 -0.494800E-04  0.805596E-11
       METHANOL        0.421475E-03  0.421467E-03  0.00000       0.173937E-04
       HCL             0.00000       0.00000       0.00000       0.00000
       SALICYLI        0.00000       0.198000E-05  0.198000E-05 -0.666502E-09
       WATER           0.00000       0.494753E-04  0.494800E-04  0.955102E-04
       SODIU-01        0.00000       0.00000       0.00000       0.00000
       NA+             0.00000       0.00000       0.00000       0.00000
       H3O+            0.00000       0.00000       0.00000       0.00000
       NAOH:(S)        0.00000       0.00000       0.00000       0.00000
       NAOH(S)         0.00000       0.00000       0.00000       0.00000
       OH-             0.00000       0.00000       0.00000       0.00000
       HBAS            0.00000       0.401638E-04  0.00000      -1.00000
    TOTAL BALANCE
    MOLE(KMOL/HR )     0.531475E-03  0.530472E-03 -0.990000E-06  0.240554E-04
    MASS(KG/HR   )     0.208319E-01  0.208315E-01                0.164811E-04
    ENTHALPY(KW      ) -0.305874E-01 -0.297472E-01               -0.274675E-01
```

Figure D.3: Mass balance lab scale

```
OVERALL FLOWSHEET BALANCE
-------------------------

                  ***  MASS AND ENERGY BALANCE  ***
                        IN            OUT         GENERATION    RELATIVE DIFF.
    CONVENTIONAL COMPONENTS
          (KMOL/HR )
       O2              0.771904E-01  0.122234E-01 -0.649661E-01  0.121057E-04
       HBA             0.00000       0.944327E-02  0.611430E-01  5.47477
       P-CRESOL        0.643611E-01  0.669355E-03 -0.636917E-01  0.146159E-10
       METHANOL        0.542410      0.542401      0.00000       0.173938E-04
       HCL             0.00000       0.00000       0.00000       0.00000
       SALICYLI        0.00000       0.254870E-02  0.254870E-02  0.170158E-15
       WATER           0.00000       0.636855E-01  0.636917E-01  0.976168E-04
       SODIU-01        0.00000       0.00000       0.00000       0.00000
       NA+             0.00000       0.00000       0.00000       0.00000
       H3O+            0.00000       0.00000       0.00000       0.00000
       NAOH:(S)        0.00000       0.00000       0.00000       0.00000
       NAOH(S)         0.00000       0.00000       0.00000       0.00000
       OH-             0.00000       0.00000       0.00000       0.00000
       HBAS            0.00000       0.516997E-01  0.00000      -1.00000
    TOTAL BALANCE
    MOLE(KMOL/HR )     0.683962      0.682671     -0.127435E-02  0.242496E-04
    MASS(KG/HR   )     26.8100       26.8096                     0.165685E-04
    ENTHALPY(KW      ) -39.3647      -38.2840                    -0.274549E-01
```

Figure D.4: Mass balance industrial scale

Figure D.5: Stream table lab scale. Stream names/numbers corresponding to Figure D.2. (Table is printed rotated 90° on the page.)

	1	2	3	4	5	6	7	8	9	10	11	12 CRESOL	HBA	MEOH1	MEOH2	MEOHRECY	OXYGEN	PURGE
Block (from)	B10	B9	B13	B13	B7	B3	B4	B12	B5	B5	B2	B1	B2	B1	B6	B1	B1	B6
Block (to)	B1	B11	B11	B9	B13	B7	B3	B4	B12	B12	B5				B4	B6		
Phase	MIXED	VAPOR	LIQUID	VAPOR	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID	MIXED	LIQUID	MIXED	LIQUID	MIXED	MIXED	VAPOR	MIXED
Mass Flow kg/hr																		
O2	4,66E-03	4,66E-03	2,13E-07	4,66E-03	2,13E-07	4,66E-03	4,66E-03	3,05E-03	2,67E-12	2,67E-12	2,67E-12	0	2,67E-12	0	3,05E-03	2,74E-03	1,92E-03	3,05E-04
HBA	5,22E-08	3,89E-11	5,22E-08	3,89E-11	5,22E-08	5,22E-08	5,22E-08	5,80E-03	5,80E-03	5,80E-03	8,96E-04	0	1,59E-07	0	5,80E-08	5,22E-08	0	5,80E-09
P-CRESOL	5,41E-03	4,78E-04	4,93E-03	4,78E-04	4,93E-03	5,41E-03	5,41E-03	5,62E-05	5,62E-05	5,62E-05	5,62E-05	5,41E-03	9,98E-09	0	0	0	0	0
METHANOL	0,123897	0,118046	5,85E-03	0,118046	5,85E-03	0,123897	0,123897	0,123897	1,24E-03	1,24E-03	1,24E-03	0	2,20E-07	0,013505	0,122658	0,110392	0	0,012266
HCL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SALICYLI	0	0	0	0	0	0	0	2,73E-04	2,73E-04	2,73E-04	2,73E-04	0	4,85E-08	0	0	0	0	0
WATER	2,08E-03	1,82E-03	2,61E-04	1,82E-03	2,61E-04	2,08E-03	2,08E-03	2,97E-03	6,60E-04	6,60E-04	6,60E-04	0	1,17E-07	0	2,31E-04	2,08E-03	0	2,31E-04
HBAS	0	0	0	0	0	0	0	0	0	0	4,90E-03	0	4,86E-03	0	0	0	0	0
Mass Frac																		
O2	0,034284	0,03731	1,93E-05	0,03731	1,93E-05	0,034284	0,034284	0,022413	3,33E-10	3,33E-10	3,33E-10	0	5,50E-10	0	0,023819	0,023819	1	0,023819
HBA	3,84E-07	3,12E-10	4,72E-06	3,12E-10	4,72E-06	3,84E-07	3,84E-07	0,042639	0,722429	0,722429	0,111576	0	3,27E-05	0	4,53E-07	4,53E-07	0	4,53E-07
P-CRESOL	0,039743	3,82E-03	0,446457	3,82E-03	0,446457	0,039743	0,039743	4,13E-04	7,00E-03	7,00E-03	7,00E-03	1	2,06E-06	0	0	0	0	0
METHANOL	0,91068	0,944313	0,529891	0,944313	0,529891	0,91068	0,91068	0,91068	0,154299	0,154299	0,154299	0	4,53E-05	1	0,958122	0,958123	0	0,958122
HCL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SALICYLI	0	0	0	0	0	0	0	2,01E-03	0,034059	0,034059	0,034059	0	1,00E-05	0	0	0	0	0
WATER	0,015293	0,014557	0,023628	0,014557	0,023628	0,015293	0,015293	0,021845	0,08221	0,08221	0,08221	0	2,41E-05	0	0,018059	0,018058	0	0,018059
HBAS	0	0	0	0	0	0	0	0	0	0	0,610853	0	0,999886	0	0	0	0	0
Total Flow kmol/hr	4,18E-03	3,94E-03	2,43E-04	3,94E-03	2,43E-04	4,18E-03	4,18E-03	4,18E-03	1,25E-04	1,25E-04	1,25E-04	5,00E-05	3,98E-05	4,21E-04	4,05E-03	3,65E-03	6,00E-05	4,05E-04
Total Flow kg/hr	0,136048	0,125007	0,011041	0,125007	0,011041	0,136048	0,136048	0,136048	8,03E-03	8,03E-03	8,03E-03	5,41E-03	4,86E-03	0,013505	0,128019	0,115217	1,92E-03	0,012802
Total Flow cum/hr	0,071543	0,110807	1,26E-05	0,048048	1,26E-05	0,045295	0,115873	1,88E-03	7,49E-06	6,98E-06	6,79E-06	5,25E-06	3,66E-06	1,72E-05	0,079624	0,071662	1,47E-03	7,96E-03
Temperature C	64,2915	70	70	167,3977	3	3	75	75	86,9546	5	5	25	5	25	64,30087	64,30087	25	64,30087
Pressure bar	1	1	1	3	3	3	1,01325	3	1	1	1	1,01325	1	1,01325	1	1	1,01325	1
Vapor Frac	0,60974	1	0	1	0	0,997504	0,970769	0,042313	0	0	0	0	0	0	0,7	0,7	1	0,7
Liquid Frac	0,39026	0	1	0	1	2,50E-03	0,029231	0,957687	1	1	0,679482	1	3,80E-04	1	0,3	0,3	0	0,3
Solid Frac	0	0	0	0	0	0	0	0	0	0	0,320518	0	0,99962	0	0	0	0	0
Enthalpy J/kmol	-2,07E+08	-1,93E+08	-2,26E+08	-1,88E+08	-2,26E+08	-1,90E+08	-1,93E+08	-2,30E+08	-2,59E+08	-2,75E+08	-1,87E+08	-1,85E+08	-2,99E+06	-2,39E+08	-2,07E+08	-2,07E+08	1,86E-09	-2,07E+08
Enthalpy J/kg	-6,35E+06	-6,07E+06	-4,97E+06	-5,92E+06	-4,97E+06	-5,84E+06	-5,94E+06	-7,06E+06	-4,05E+06	-4,30E+06	-2,91E+06	-1,71E+06	-24470,8	-7,47E+06	-6,55E+06	-6,55E+06	5,82E-11	-6,55E+06
Enthalpy kW	-0,240087	-0,210742	-0,015234	-0,205408	-0,015233	-0,220641	-0,224468	-0,266853	-9,03E-03	-9,58E-03	-6,49E-03	-2,56E-03	-3,30E-05	-0,028024	-0,232779	-0,2095	3,10E-20	-0,023278
Entropy J/kmol-K	-1,58E+05	-1,14E+05	-2,53E+05	-1,11E+05	-2,53E+05	-1,19E+05	-1,19E+05	-2,15E+05	-2,16E+05	-2,68E+05	-1,58E+05	-4,50E+05	-10095,69	-2,42E+05	-1,48E+05	-1,48E+05		-1,48E+05
Entropy J/kg-K	-4855,451	-3598,179	-5557,449	-3489,394	-5556,533	-3640,553	-3641,66	-6592,061	-3373,648	-4180,103	-2471,72	-4160,026	-82,68991	-7557,247	-4685,299	-4685,299		-4685,299
Density kmol/cum	0,058398	0,035514	19,25532	0,081903	19,25255	0,092238	0,036056	2,221048	16,71961	17,95036	18,45779	9,53273	10,88117	24,49797	0,050884	0,050884	0,040875	0,050884
Density kg/cum	1,901637	1,128149	876,1165	2,60133	875,9904	3,003604	1,174119	72,34251	1071,374	1150,239	1182,755	1030,869	1328,493	784,9677	1,607788	1,607788	1,307941	1,607788
Average MW	32,56362	31,7659	45,49998	31,7659	45,49998	32,56362	32,56362	32,57134	64,07889	64,07889	64,07889	108,1399	122,091	32,04216	31,59687	31,59689	31,9988	31,59687
Liq Vol 60F cum/hr	1,71E-04	1,59E-04	1,24E-05	1,59E-04	1,24E-05	1,71E-04	1,71E-04	1,69E-04	7,28E-06	7,28E-06	7,28E-06	5,22E-06	4,01E-06	1,70E-05	1,62E-04	1,46E-04	3,21E-06	1,62E-05

Figure D.5: Stream table lab scale, stream names/numbers corresponding to Figure D.2

Figure D.6 — Stream table (industrial scale). Stream names/numbers correspond to Figure D.2.

	1	2	3	4	5	6	7	8	9	10	11	12 CRESOL	HBA	MEOH1	MEOH2	MEOHRECY	OXYGEN	PURGE
	B10	B9	B13	B13	B7	B3	B4	B12	B5	B5	B2	B1	B2	B1	B6	B1	B1	B6
	B1	B10	B11	B9	B13	B7	B3	B4	B12	B12	B5				B4	B6		
	MIXED	LIQUID	VAPOR	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID	LIQUID	MIXED	LIQUID	MIXED	LIQUID	MIXED	MIXED	VAPOR	MIXED
Mass Flow kg/hr																		
O2	4,66E-03	2,13E-07	4,66E-03	2,13E-07	4,66E-03	4,66E-03	4,66E-03	3,05E-03	2,67E-12	2,67E-12	2,67E-12	2,67E-12	2,67E-12	0	3,05E-03	2,74E-03	1,92E-03	3,05E-04
HBA	5,22E-08	5,22E-08	3,89E-11	5,22E-08	5,22E-08	5,22E-08	5,22E-08	5,80E-03	5,80E-03	5,80E-03	8,96E-04	8,96E-04	1,59E-07	0	5,80E-08	5,22E-08	0	5,80E-09
P-CRESOL	5,41E-03	4,93E-03	4,78E-04	4,93E-03	5,41E-03	5,41E-03	5,41E-03	5,62E-05	5,62E-05	5,62E-05	5,62E-05	5,41E-03	2,06E-06	0	0	0	0	0
METHANOL	0,123897	5,85E-03	0,118046	5,85E-03	0,123897	0,123897	0,123897	0,123897	1,24E-03	1,24E-03	1,24E-03	0	2,20E-07	0,013505	0,122658	0,110392	0	0,012266
HCL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SALICYLI	0	0	0	0	0	0	0	0	0	0	0	0	4,85E-08	0	0	0	0	0
WATER	2,08E-03	2,61E-04	1,82E-03	2,61E-04	2,08E-03	2,08E-03	2,97E-03	2,97E-03	6,60E-04	6,60E-04	6,60E-04	0	1,17E-07	0	2,31E-03	2,08E-03	0	2,31E-04
HBAS	0	0	0	0	0	0	0	0	0	0	4,90E-05	0	4,86E-03	0	0	0	0	0
Mass Frac																		
O2	0,034284	1,93E-05	0,03731	1,93E-05	0,034284	0,034284	0,034284	0,022413	3,33E-10	3,33E-10	3,33E-10	8,42E-10	5,50E-10	0	0,023819	0,023819	1	0,023819
HBA	3,84E-07	4,72E-06	3,12E-10	4,72E-06	3,84E-07	3,84E-07	3,84E-07	0,042639	0,722429	0,722429	0,111576	0,282288	3,27E-05	0	4,53E-07	4,53E-07	0	4,53E-07
P-CRESOL	0,039743	0,446457	3,82E-03	0,446457	0,039743	0,039743	0,039743	4,13E-04	7,00E-03	7,00E-03	7,00E-03	0,017718	2,06E-06	0	0	0	0	0
METHANOL	0,91068	0,529891	0,944313	0,529891	0,91068	0,91068	0,91068	0,91068	0,154299	0,154299	0,154299	0,390376	4,53E-05	1	0,958122	0,958123	0	0,958122
HCL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SALICYLI	0	0	0	0	0	0	0	2,01E-03	0	0	0	1,00E-05	1,00E-05	0	0	0	0	0
WATER	0,015293	0,023628	0,014557	0,023628	0,015293	0,015293	0,021845	0,021845	0,08221	0,08221	0,08221	0,207992	2,41E-05	0	0,018059	0,018058	0	0,018059
HBAS	0	0	0	0	0	0	0	0	0	0	0,015457	0,015457	0,999886	0	0	0	0	0
Total Flow kmol/hr	4,18E-03	2,43E-04	3,94E-03	2,43E-04	4,18E-03	4,18E-03	4,18E-03	4,18E-03	1,25E-04	1,25E-04	8,55E-05	5,00E-05	3,98E-05	4,21E-04	4,05E-03	3,65E-03	6,00E-05	4,05E-04
Total Flow kg/hr	0,136048	0,011041	0,125007	0,011041	0,136048	0,136048	0,136048	0,136048	8,03E-03	8,03E-03	3,17E-03	5,41E-03	4,86E-03	0,013505	0,128019	0,115217	1,92E-03	0,012802
Total Flow cum/hr	0,071543	1,26E-05	0,110807	1,26E-05	0,045295	0,045295	0,115873	0,048048	7,49E-06	6,98E-06	6,79E-06	5,25E-06	3,66E-06	1,72E-05	0,079624	0,071662	1,47E-03	7,96E-03
Temperature C	64,2915	70	70	70,10658	119,0087	119,0087	75	75	86,9546					25	64,30087	64,30087	25	64,30087
Pressure bar	1	1,01325	1,01325	1	3	1,01325	1,01325	3	1	1,01325	1	1,01325	1	1,01325	1	1	1,01325	1
Vapor Frac	0,60974	0	1	0	0,997504	0,970769	0,957687	0,042313	0	0	0	0	0	0	0,7	0,7	1	0,7
Liquid Frac	0,39026	1	0	1	2,50E-03	0,029231	0,042313	0,957687	1	1	0,679482	1	0,99962	1	0,3	0,3	0	0,3
Solid Frac	0	0	0	0	0	0	0	0	0	0	0,320518	0	3,80E-04	0	0	0	0	0
Enthalpy J/kmol	-2,07E+08	-2,26E+08	-1,88E+08	-2,26E+08	-1,90E+08	-1,93E+08	-2,30E+08	-2,59E+08	-2,75E+08	-2,75E+08	-1,87E+08	-1,85E+08	-2,99E+08	-2,39E+08	-2,07E+08	-2,07E+08	1,86E-09	-2,07E+08
Enthalpy J/kg	-6,35E+06	-4,97E+06	-5,92E+06	-4,97E+06	-5,84E+06	-5,94E+06	-7,06E+06	-4,05E+06	-4,30E+06	-4,30E+06	-7,30E+06	-1,71E+06	-24470,8	-7,47E+06	-6,55E+06	-6,55E+06	5,82E-11	-6,55E+06
Enthalpy kW	-0,240087	-0,015234	-0,205408	-0,015233	-0,220641	-0,224468	-0,266853	-9,03E-03	-9,58E-03	-9,58E-03	-6,49E-03	-2,56E-03	-3,30E-05	-0,028024	-0,232779	-0,2095	3,10E-20	-0,023278
Entropy J/kmol-K	-1,58E+05	-2,53E+05	-1,11E+05	-2,53E+05	-1,19E+05	-1,19E+05	-2,15E+05	-2,16E+05	-2,68E+05	-2,68E+05	-1,58E+05	-4,50E+05	-10095,69	-2,42E+05	-1,48E+05	-1,48E+05	0	-1,48E+05
Entropy J/kg-K	-4855,451	-5557,449	-3489,394	-5556,533	-3640,553	-3641,66	-6592,061	-3373,648	-4180,103	-4180,103	-2471,72	-4160,026	-82,68991	-7557,247	-4685,299	-4685,299	-4685,299	-4685,299
Density kmol/cum	0,058398	19,25532	0,035514	19,25255	0,092238	0,036056	0,036056	0,081903	16,71961	17,95036	18,45779	9,53273	10,88117	24,49797	0,050884	0,050884	0,040875	0,050884
Density kg/cum	1,901637	876,1165	1,128149	875,9904	3,003604	1,174119	2,221048	2,60173	1071,374	1150,239	1182,755	1030,869	1328,493	784,9677	1,607788	1,607788	1,307941	1,607788
Average MW	32,56362	45,49998	31,7659	45,49998	32,56362	32,56362	32,57134	32,57134	64,07889	64,07889	37,09987	108,1399	122,091	32,04216	31,59687	31,59689	31,9988	31,59687
Liq Vol 60F cum/hr	1,71E-04	1,24E-05	1,59E-04	1,24E-05	1,71E-04	1,71E-04	1,69E-04	1,69E-04	7,28E-06	7,28E-06	7,28E-06	5,22E-06	4,01E-06	1,70E-05	1,62E-04	1,46E-04	3,21E-06	1,62E-05

Figure D.6: Stream table industrial scale, stream names/numbers corresponding to Figure D.2

D.4 Cost Estimation

The catalyst recovery is not taken into account, it was assumed that the catalyst was refreshed every once in a while, giving an amount of catalyst supplied per year as visible in Table D.4. These recovery costs can be taken into account when this is desired.

The constants for the equipment in the HBA process are taken from Towler and Sinnott and shown in Table D.1.

Equipment	Detailed description	a	b	n
Compressor	Reciprocating compressor	260,000	2,700	0.75
Reactor	Jacketed, agitated	61,500	32,500	0.8
Distillation column				
	- Pressure vessel vertical	11,600	34	0.85
	- Sieve trays	130	440	1.8
Centrifuge	High speed disk	57,000	480,000	0.7
Crystallizer	Scraped surface crystallizer	10,000	13,200	0.8
Cooler	Packaged mechanical refrigerator evaporator	24,000	3,500	0.9

Table D.1: Overview of the equipment parameters [62]

The S values for the equipment is shown in Table D.2 together with the calculated costs. In some cases, for example the compressor, the lab parameter and industry parameter were because of the minimum value the same.

Equipment	Size Unit	S lab	S industry	C_e lab	C_e industry
Compressor	kW	93	93	$340,858.55	$340,858.55
Reactor	m^3	0.5	5	$80,166.35	$179,276.70
Distillation column					
	kg (shell mass)	160	160	$14,140.86	$14,140.86
	m (diameter)	0.5	0.5	$256.36	$256.36
Centrifuge	m (diameter)	0.26	0.3	$243,948.76	$263,645.58
Crystallizer	m (length)	7	10	$72,611.25	$93,286.37
Cooler	kW	50	50	$142,341.58	$142,341.58

Table D.2: Overview of the equipment costs

Table D.3 gives an overview of the fixed capital costs. An example calculation for the industrial equipment costs from Table D.3 with the CEPCI correction:

$$\text{Cost in 2018} \ = \ \$1,033,807.00 \ \times \ \frac{603.1}{532.9} \ = \ \$1,169,992.50$$

The ISBL, OSBL, Engineering costs and Contingency of the HBA process are shown in Table D.3.

More details of the cost estimation can be seen in Figures D.7 and D.8, which are based on a template with assumptions of Towler and Sinnott [62].

In order to calculate the variable costs per year, the price of the raw materials has to be known, as well as the amount necessary per year. The price is based on a bulk supply buy, but it should be stated that often this data is not freely available, so it also is an estimation. The price in USDollar per year per product is given in Figures D.7 and D.8.

Besides the raw material costs, there are also costs from the waste streams, in this case mainly the aqueous waste stream. The price per kg for dealing with this waste is set to -1.50. Another part of the variable costs is the utilities. For lab scale, these are set to 2% of the cash cost of production (CCOP), since the operation on this scale does not require a lot of energy. For the industrial scale, the utilities make up of 10% of the CCOP.

	Lab	Industry	Remarks
Total C_e	$894,324.71	$1,033,807.00	Adding all C_e equipment costs
2018 corrected	$1,012,135.92	$1,169,992.50	Corrected with CEPCI value of 2018 (most recent)
ISBL fixed capital costs	$3,674,053.40	$4,247,072.76	Multiply with Lang Factor (3.63)
OSBL fixed capital costs	$734,810.68	$1,698,829.11	20% of ISBL for lab scale, 40% of industrial scale
Engineering costs	$440,886.41	$594,590.19	10% of ISBL and OSBL
Contingency	$661,329.61	$891,885.28	15% of ISBL and OSBL
Total Fixed Capital Cost	$5,511,080.09	$7,432,377.33	Adding ISBL, OSBL, Engineering and Contingency

Table D.3: Overview of the costs

Chemical	Price ($/kg)	Mass flow lab (kg/year)	Mass flow industry (kg/year)	Reference
Pine Wood	0.077	527.34	610,352	[49], [107]
Cresol		43.26	55,674	
Oxygen	0.01	15.36	19,769	[108]
Methanol	0.36	108.04	139,057	[109], [110]
Hydrochloric acid	0.40	26.22	33,751	[111]
NaOH	1.00	12.27	15,788	[112]
CuMn				
Cu	42.42	0.0064	8.24	[113]
Mn	66.67	0.0016	2.06	[114]

Table D.4: Overview of the raw material costs

The only costs that need to be added to the cost estimation are those of the pyrolysis process, so from pine wood to cresol. It was already explained that this was done based on the data and percentages of the BTG Group [49]. Namely 43% of the costs of this process part are made up of the biomass costs. Those costs can be calculated since the price of the pine wood is known ($0.077/kg, or $77/ton) and the amount needed as well (610,352 kg/year, see Table D.4. Therefore the total costs of the biomass pyrolysis are roughly estimated according to the example in equation D.1:

$$\text{Pyrolysis Process Production Costs} = \frac{610,352 \times 0.077}{43} \times 100 = \$106,020.85 \qquad \text{(D.1)}$$

Then the only remaining part in the cost analysis are the yields of the product and the side product. The price of the side product should be critically considered since this price seems too high for the applications compared with 4-hydroxybenzaldehyde. However this value was the one that made the most sense compared with all considered sources.

Chemical	Price ($/kg)	Mass flow lab (kg/year)	Mass flow industry (kg/year)	Reference
4-hydroxybenzaldehyde	50	38.847	50,000	[81]
4-hydroxybenzoic acid	96.90	2.187	2,815	[115]

Table D.5: Overview of the products

The previous tables are all part of the cost analysis overviews in Figures D.7 and D.8 on the following pages.

Production of 4-hydroxybenzaldehyde from the pyrolysis of pine wood

COST OF PRODUCTION

Capital Cost Basis Year   2018
On stream   8000 hr/yr   333.33 day/yr

YIELD ESTIMATE	CAPITAL COSTS	
		$MM
Yield information taken from ASPEN Pro simulation environment,	ISBL Capital Cost	3.674
Based on theoretical values of the article published by Wang, Yang, Zhang, Wu and Xu (2004).	OSBL Capital Cost	0.735
	Engineering Costs	0.441
Scale of production set to lab scale: 38.8 kg/yr	Contingency	0.661
	Total Fixed Capital Cost	5.511
Pyrolysis process costs based on data from the BTG Group	Working Capital	0.276

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
4-hydroxybenzaldehyde	kg	1	39	50	0.002	50.00
Total Key Product Revenues (REV)	kg	1	39		0.002	50.00

By-products & Waste Streams						
4-hydroxybenzoic acid	kg	0.056	2	96.90	0.000212	5.46
Aqueous Waste	kg	0.136	5	-1.50	-0.000008	-0.20
Total Byproducts and Wastes (BP)	kg	0.192	7		0.00	5.25

Raw Materials						
Pine Wood	kg	13.57528958	527	0.08	0.00	1.05
Oxygen	kg	0.3953667954	15	0.01	0.0000	0.00
Hydrochloric acid	kg	0.6749034749	26	0.40	0.0000	0.27
Total Raw Materials (RM)	kg	14.64555985	569		0.000051	1.32
			Gross Margin (GM = REV + BP - RM)		0.00	53.93

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
Methanol	kg	2.78	108	0.36	0.0000389	1.00
Sodium hydroxide	kg	0.316	12.267	1.00	0.0000123	0.32
Cu	kg	0.0002	0.0064	42.42	0.0000003	0.01
Mn	kg	4.12E-05	0.0016	66.67	0.0000001	0.00
Total Consumables (CONS)					0.00	1.33

Variable Cost of Production

			$MM/yr	$/unit product
Utilities	2% of Cash Cost of Production		0.025	648.90
	Variable Cost of Production (VCOP = RM - BP + CONS + UTS)		0.025	646.29

FIXED OPERATING COSTS

			$MM/yr	$/unit product
Labor				
4.8 Operators per Shift Position				
Number of shift position	3	30,000 $/yr each	0.43	11,119.69
Supervision		25% of Operating Labor	0.11	2,779.92
Direct Ovhd.		45% of Labor & Superv.	0.24	6,254.83
Maintenance		3% of ISBL Investment	0.11	2,837.11
Overhead Expense				
Plant Overhead		30% of Labor & Maint.	0.27	6,897.46
Tax & Insurance		2% of Fixed Investment	0.08	2,127.83
Interest on Debt Financing		0% of Fixed Capital	0.00	0.00
		6% of Working Capital	0.02	425.57
		Fixed Cost of Production (FCOP)	1.26	32,442.41

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	5.511	15%	15	0.171	0.94	24,259.68
				Total Annual Capital Charge	0.94	24,259.68

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	0.0251	646.29
Fixed Cost of Production	1.26	32,442.41
Cash Cost of Production	1.29	33,088.70
Pyrolysis Process Production Costs	9.44E-05	2.43
Gross Profit	-1.28	-33041.13
Total Cost of Production	2.23	57,350.81

Figure D.7: Economic Analysis of p-hydroxybenzaldehyde production (lab scale)

Production of 4-hydroxybenzaldehyde from the pyrolysis of pine wood

COST OF PRODUCTION

Capital Cost Basis Year	2018
On stream	8000 hr/yr 333.33 day/yr

YIELD ESTIMATE

Yield information taken from ASPEN Pro simulation environment,
Based on theoretical values of the article published by Wang, Yang, Zhang, Wu and Xu (2004).

Scale of production set to 50 ton/year

Pyrolysis process costs based on data from the BTG Group

CAPITAL COSTS

	$MM
ISBL Capital Cost	4.247
OSBL Capital Cost	1.699
Engineering Costs	0.595
Contingency	0.892
Total Fixed Capital Cost	7.432
Working Capital	0.372

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
4-hydroxybenzaldehyde	kg	1	50,000	50	2.500	50.00
Total Key Product Revenues (REV)	kg	1	50,000		2.500	50.00
By-products & Waste Streams						
4-hydroxybenzoic acid	kg	0.056	2,815	96.90	0.272812	5.46
Aqueous Waste	kg	0.184	9,200	-1.50	-0.013800	-0.28
Total Byproducts and Wastes (BP)	kg	0.240	12,015		0.26	5.18
Raw Materials						
Pine Wood	kg	12.20704	610,352	0.08	0.05	0.94
Oxygen	kg	0.3953816	19,769	0.01	0.0002	0.00
Hydrochloric acid	kg	0.6750112	33,751	0.40	0.0135	0.27
Total Raw Materials (RM)	kg	13.2774328	663,872		0.06	1.21
Gross Margin (GM = REV + BP - RM)					2.70	53.97

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
Methanol	kg	2.781138	139,057	0.36	0.0500605	1.00
Sodium hydroxide	kg	0.315769	15,788.45	1.00	0.02	0.32
Cu	kg	0.0001648	8.2400	42.42	0.0003495	0.01
Mn	kg	0.0000412	2.0600	66.67	0.0001373	0.00
Total Consumables (CONS)					0.05	1.01

Variable Cost of Production

		$MM/yr	$/unit product
Utilities	10% of Cash Cost of Production	0.15	3.03
Variable Cost of Production (VCOP = RM - BP + CONS + UTS)		0.00	0.08

FIXED OPERATING COSTS

			$MM/yr	$/unit product
Labor				
4.8 Operators per Shift Position				
Number of shift position	3	30,000 $/yr each	0.43	8.64
Supervision		25% of Operating Labor	0.11	2.16
Direct Ovhd.		45% of Labor & Superv.	0.24	4.86
Maintenance		3% of ISBL Investment	0.13	2.55
Overhead Expense				
Plant Overhead		30% of Labor & Maint.	0.27	5.46
Tax & Insurance		2% of Fixed Investment	0.11	2.23
Interest on Debt Financing		0% of Fixed Capital	0.00	0.00
		6% of Working Capital	0.02	0.45
Fixed Cost of Production (FCOP)			1.32	26.35

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	7.432	15%	15	0.171	1.27	25.42
Total Annual Capital Charge					1.27	25.42

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	0.004	0.08
Fixed Cost of Production	1.32	26.35
Cash Cost of Production	1.32	26.43
Pyrolysis Process Production Costs	0.109	2.19
Gross Profit	1.069	21.39
Total Cost of Production	2.70	54.03
Payback Time	6.9	year

Figure D.8: Economic Analysis of p-hydroxybenzaldehyde production (industrial scale)

E BTX / toluene process design

E.1 Input

	Reaction equation	Activation energy (eV)	k^+-value (s^{-1})	k^--value (s^{-1})
Eq. 4.3	$C_7H_8O + H_2 \rightarrow C_7H_8 + H_2O$	1.23	1.9	6.2×10^6
Eq. 4.6	$C_7H_8O + 3\,H_2 \rightarrow C_7H_{14}O$	1.45	70	7.4×10^{-2}
Eq. 4.7	$C_7H_{14}O \rightarrow C_7H_8 + H_2O + 2\,H_2$	0.92	150,000	6.5×10^{-6}

Table E.1: Overview of the main reactions and kinetic constants

E.2 Aspen Plus$^{\text{TM}}$ diagram
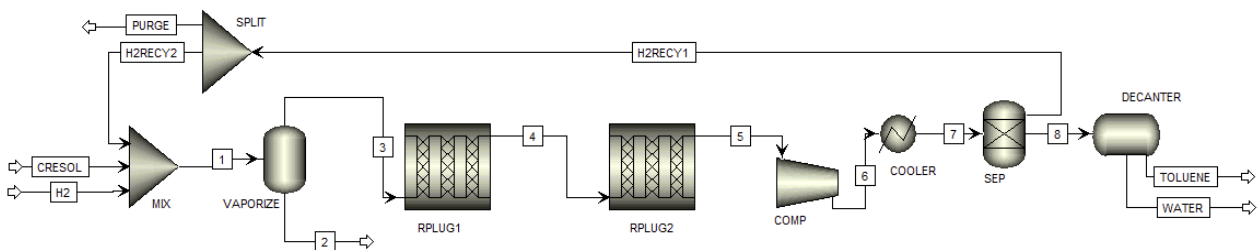
Figure E.1: Aspen Plus$^{\text{TM}}$ Model

E.3 Aspen Plus$^{\text{TM}}$ results


```
OVERALL FLOWSHEET BALANCE
-------------------------

              ***  MASS AND ENERGY BALANCE  ***
                    IN          OUT        GENERATION   RELATIVE DIFF.
CONVENTIONAL COMPONENTS
     (KMOL/HR )
  TOLUENE        0.00000     0.461689E-02  0.461690E-02  0.753306E-06
  BENZENE        0.00000     0.00000       0.00000       0.00000
  MCONE          0.00000     0.00000       0.00000       0.00000
  MCRESOL        0.462364E-02 0.00000     -0.462364E-02  0.187593E-15
  COL            0.00000     0.712781E-05  0.712786E-05  0.730691E-05
  CYCHEXEN       0.00000     0.00000       0.00000       0.00000
  MCYCHEXA       0.00000     0.00000       0.00000       0.00000
  VINCYHEX       0.00000     0.00000       0.00000       0.00000
  H2             0.406770E-01 0.360379E-01 -0.463828E-02  0.209364E-04
  WATER          0.00000     0.461687E-02  0.461690E-02  0.664410E-05
TOTAL BALANCE
  MOLE(KMOL/HR ) 0.453007E-01 0.452788E-01 -0.209978E-04  0.195546E-04
  MASS(KG/HR  )  0.582000     0.582039                   -0.672168E-04
  ENTHALPY(KW  ) -0.250675    -0.358607                    0.300977
```

Figure E.2: Lab scale

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OVERALL FLOWSHEET BALANCE
-------------------------

              ***  MASS AND ENERGY BALANCE  ***
                    IN          OUT        GENERATION   RELATIVE DIFF.
CONVENTIONAL COMPONENTS
     (KMOL/HR )
  TOLUENE        0.00000     13.5845      13.5845       -0.256926E-06
  BENZENE        0.00000     0.00000      0.00000        0.00000
  MCONE          0.00000     0.00000      0.00000        0.00000
  MCRESOL        13.6015     0.00000     -13.6015        0.00000
  COL            0.00000     0.170868E-01 0.170868E-01 -0.387479E-06
  CYCHEXEN       0.00000     0.00000      0.00000        0.00000
  MCYCHEXA       0.00000     0.00000      0.00000        0.00000
  VINCYHEX       0.00000     0.00000      0.00000        0.00000
  H2             119.661     106.033     -13.6357       -0.618357E-04
  WATER          0.00000     13.5845      13.5845        0.144428E-05
TOTAL BALANCE
  MOLE(KMOL/HR ) 133.262     133.219     -0.512309E-01 -0.554034E-04
  MASS(KG/HR  )  1712.09     1712.11                    -0.105665E-04
  ENTHALPY(KW  ) -737.419    -1054.72                    0.300837
```

Figure E.3: Industrial scale

Figure E.4: Stream table lab scale, stream names/numbers corresponding to Figure E.1

	1	2	3	4	5	6	7	8	CRESOL	H2	H2RECY1	H2RECY2	PURGE	TOLUENE	WATER
	VAPORIZE	RPLUG1	RPLUG1	RPLUG2	COMP	COOLER	SEP	DECANTER	MIX	MIX	SPLIT	MIX	SPLIT	DECANTER	DECANTER
	MIX	VAPORIZE		RPLUG1	RPLUG2	COMP	COOLER	SEP			SEP	SPLIT			
	MIXED	MISSING	VAPOR	VAPOR	VAPOR	VAPOR	MIXED	LIQUID	LIQUID	VAPOR	MIXED	MIXED	MIXED	LIQUID	LIQUID
Substream: MIXED															
TOLUENE	4,19E-05	0	4,19E-05	1,64E-04	4,66E-03	4,66E-03	4,66E-03	4,61E-03		0	4,66E-05	4,19E-05	4,66E-06	4,61E-03	5,61E-07
MCRESOL	4,62E-03	0	4,62E-03	0	0	0	0	0	4,62E-03	0	0	0	0	0	0
COL	6,47E-08	0	6,47E-08	4,50E-03	7,19E-06	7,19E-06	7,19E-06	7,12E-06	0	0	7,19E-08	6,47E-08	7,19E-09	3,63E-06	3,50E-06
H2	0,364693	0	0,364693	0,351066	0,360055	0,360055	0,360055	3,60E-05	0	0,040677	0,360019	0,324016	0,036002	1,83E-05	1,77E-05
WATER	4,57E-04	0	4,57E-04	5,79E-04	5,07E-03	5,07E-03	5,07E-03	4,57E-03	0	0	5,07E-04	4,57E-04	5,07E-05	9,55E-06	4,56E-03
Mass Flow kg/hr															
TOLUENE	3,86E-03	0	3,86E-03	0,015122	0,429266	0,429266	0,429266	0,424974	0	0	4,29E-03	3,86E-03	4,29E-04	0,424922	5,17E-05
MCRESOL	0,5	0	0,5	0	0	0	0	0	0,5	0	0	0	0	0	0
COL	7,39E-06	0	7,39E-06	0,514061	8,21E-04	8,21E-04	8,21E-04	8,13E-04	0	0	8,21E-06	7,39E-06	8,21E-07	4,14E-04	3,99E-04
H2	0,735178	0	0,735178	0,707706	0,725827	0,725827	0,725827	7,26E-05	0	0,082	0,725755	0,653178	0,072575	3,70E-05	3,56E-05
WATER	8,23E-03	0	8,23E-03	0,010427	0,0914	0,0914	0,0914	0,08226	0	0	9,14E-03	8,23E-03	9,14E-04	1,72E-04	0,082088
Mass Frac															
TOLUENE	3,10E-03	0	3,10E-03	0,012124	0,344152	0,344152	0,344152	0,836366	0	0	5,81E-03	5,81E-03	5,81E-03	0,998536	6,26E-04
MCRESOL	0,400874	0	0,400874	0	0	0	0	0	1	0	0	0	0	0	0
COL	5,92E-06	0	5,92E-06	0,412134	8,21E-04	8,21E-04	6,58E-04	1,60E-03	0	0	1,11E-05	1,11E-05	1,11E-05	9,73E-04	4,83E-03
H2	0,589428	0	0,589428	0,567383	0,581912	0,581912	0,581912	1,43E-04	0	1	0,981817	0,981818	0,981817	8,68E-05	4,31E-04
WATER	6,59E-03	0	6,59E-03	8,36E-03	0,073278	0,073278	0,073278	0,161891	0	0	0,012365	0,012364	0,012365	4,04E-04	0,99411
Total Flow kmol/hr	0,369815	0	0,369815	0,35631	0,369794	0,369794	0,369794	9,22E-03	4,62E-03	0,040677	0,360573	0,324515	0,036057	4,64E-03	4,58E-03
Total Flow kg/hr	1,247274	0	1,247274	1,247315	1,247315	1,247315	1,247315	0,50812	0,5	0,082	0,739196	0,665274	0,07392	0,425545	0,082574
Total Flow cum/hr	8,528307	0	14,54826	14,01698	14,54743	1,317835	0,278351	5,42E-04	4,83E-04	1,00835	0,277653	0,249887	0,027765	4,91E-04	8,33E-05
Temperature C	7,853101		200	200	200	1012,713	5	5	25	25	5	5	5	20	20
Pressure bar	1	1	1	1	1	30	30	30	1	1	30	30	30	1	1
Vapor Frac	0,986995		1	1	1	1	0,974586	0	0	1	0,99888	0,99888	0,99888		
Liquid Frac	0,013005		0	0	0	0	0,025415	1	1	0	1,12E-03	1,12E-03	1,12E-03	1	1
Solid Frac	0		0	0	0	0	0	0	0	0	0	0	0	0	0
Enthalpy J/kmol	-3,28E+06		3,43E+06	6,71E+05	2,65E+06	2,93E+07	-4,31E+06	-1,37E+08	-1,95E+08	3,73E-09	-9,58E+05	-9,58E+05	-9,58E+05	1,05E+07	-2,85E+08
Enthalpy J/kg	-9,73E+05		1,02E+06	1,92E+05	7,86E+05	8,68E+06	-1,28E+06	-2,48E+06	-1,80E+06	1,85E-09	-4,68E+05	-4,68E+05	-4,68E+05	1,15E+05	-1,58E+07
Enthalpy kW	-0,337067		0,352597	0,066383	0,272412	3,00845	-0,443137	-0,350522	-0,250675	4,21E-17	-0,095993	-0,086393	-9,60E-03	0,013602	-0,36261
Entropy J/kmol-K	-7378,555		10984,48	6555,026	11689,51	15872,04	-35978,72	-2,62E+05	-4,48E+05	109,4414	-30329,15	-30329,11	-30329,15	-3,43E+05	-1,64E+05
Entropy J/kg-K	-2187,734		3256,888	1872,52	3465,616	4705,619	-10666,69	-4747,285	-4145,206	54,28965	-14794,28	-14794,28	-14794,28	-3737,788	-9110,466
Density kmol/cum	0,043363		0,02542	0,02542	0,02542	0,280607	1,32852	17,00231	9,57759	0,04034	1,298645	1,298646	1,298645	9,46375	54,97888
Density kg/cum	0,146251		0,085734	0,088986	0,085741	0,946488	4,481096	936,8556	1035,72	0,081321	2,662299	2,662299	2,662299	867,3473	991,6002
Average MW	3,372693		3,372693	3,500644	3,372997	3,372997	3,372997	55,10166	108,1399	2,01588	2,050059	2,050057	2,050059	91,64942	18,03602
Liq Vol 60F cum/hr	0,02003	0	0,02003	0,019394	0,01987	0,01987	0,01987	5,74E-04	4,85E-04	2,18E-03	0,019296	0,017366	1,93E-03	4,90E-04	8,37E-05

Substance: MIXED

	1 VAPORIZE MIX MIXED	2 VAPORIZE MISSING	3 RPLUG1 VAPORIZE VAPOR	4 RPLUG2 RPLUG1 VAPOR	5 COMP RPLUG2 VAPOR	6 COOLER COMP VAPOR	7 SEP COOLER MIXED	8 DECANTER SEP LIQUID	CRESOL MIX LIQUID	H2 MIX VAPOR	H2RECY1 SPLIT SEP MIXED	H2RECY2 MIX SPLIT MIXED	PURGE SPLIT MIXED	TOLUENE DECANTER LIQUID	WATER DECANTER LIQUID
Mole Flow kmol/hr															
TOLUENE	0,1234	0	0,1234	0,483039	13,71192	13,71192	13,71192	13,5748	0	0	0,137119	0,1234	0,013712	13,57315	1,65E-03
MCRESOL	13,60155	0	13,60155	0	0	0	0	0	13,60155	0	0	0	0	0	0
COL	1,91E-04	0	1,91E-04	13,25006	0,021181	0,021181	0,021181	0,020969	0	0	2,12E-04	1,91E-04	2,12E-05	0,010677	0,010292
H2	1072,741	0	1072,741	1032,632	1059,089	1059,089	1059,089	0,105909	0	119,6609	1058,984	953,0801	105,8984	0,053925	0,051984
WATER	1,343788	0	1,343788	1,703427	14,93231	14,93231	14,93231	13,43908	0	0	1,493231	1,343788	0,149323	0,028109	13,41097
Mass Flow kg/hr															
TOLUENE	11,3701	0	11,3701	44,50746	1263,423	1263,423	1263,423	1250,789	0	0	12,63423	11,3701	1,263423	1250,637	0,152106
MCRESOL	1470,87	0	1470,87	0	0	0	0	0	1470,87	0	0	0	0	0	0
COL	0,021787	0	0,021787	1512,992	2,418577	2,418577	2,418577	2,394391	0	0	0,024186	0,021787	2,42E-03	1,219144	1,175247
H2	2162,517	0	2162,517	2081,662	2134,997	2134,997	2134,997	0,2135	0	241,222	2134,784	1921,295	213,4784	0,108707	0,104793
WATER	24,20871	0	24,20871	30,68771	269,0097	269,0097	269,0097	242,1087	0	0	26,90097	24,20871	2,690097	0,506392	241,6024
Mass Frac															
TOLUENE	3,10E-03	0	3,10E-03	0,012128	0,344271	0,344271	0,344271	0,836365	0	0	5,81E-03	5,81E-03	5,81E-03	0,998536	6,26E-04
MCRESOL	0,400893	0	0,400893	0	0	0	0	1	1	0	0	0	0	0	0
COL	5,94E-06	0	5,94E-06	0,412276	6,59E-04	6,59E-04	6,59E-04	1,60E-03	0	0	1,11E-05	1,11E-05	1,11E-05	9,73E-04	4,84E-03
H2	0,589404	0	0,589404	0,567234	0,581767	0,581767	0,581767	1,43E-04	0	1	0,981806	0,981808	0,981806	8,68E-05	4,31E-04
WATER	6,60E-03	0	6,60E-03	8,36E-03	0,073303	0,073303	0,073303	0,161891	0	0	0,012372	0,012371	0,012372	4,04E-04	0,994107
Total Flow kmol/hr	1087,81	0	1087,81	1048,068	1087,755	1087,755	1087,755	27,14075	13,60155	119,6609	1060,614	954,5475	106,0614	13,66586	13,4749
Total Flow kg/hr	3668,988	0	3668,988	3669,849	3669,849	3669,849	3669,849	1495,506	1470,87	241,222	2174,343	1956,896	217,4343	1252,471	243,0345
Total Flow cum/hr	25085,88	0	42793,63	41230,22	42791,46	4203,133	818,7596	1,5963	1,420143	2966,295	816,7077	735,032	81,67077	1,444023	0,245092
Temperature C	7,852539	200	200	200	200	30	5	5	25	25	5	5	5	20	20
Pressure bar	1	1	1	1	1	1	30	30	1	1	30	30	30	1	1
Vapor Frac	0,986994		1	1	1	1	0,97457	0	0	1	0,998879	0,998879	0,998879	0	0
Liquid Frac	0,013006		0	0	0	0	0,02543	1	1	0	1,12E-03	1,12E-03	1,12E-03	1	1
Solid Frac	0		0	0	0	0	0	0	0	0	0	0	0	0	0
Enthalpy J/kmol	-3,28E+06		3,43E+06	6,68E+05	2,65E+06	3,31E+07	-4,32E+06	-1,37E+08	-1,95E+08	3,73E-09	-9,59E+05	-9,59E+05	-9,59E+05	1,05E+07	-2,85E+08
Enthalpy J/kg	-9,73E+05		1,02E+06	1,91E+05	7,86E+05	9,81E+06	-1,28E+06	-2,48E+06	-1,80E+06	1,85E-09	-4,68E+05	-4,68E+05	-4,68E+05	1,15E+05	-1,58E+07
Enthalpy kW	-991,6033		1037,078	194,4892	800,8766	9998,314	-1304,154	-1031,659	-737,4195	1,24E-13	-282,4293	-254,1838	-28,24293	40,03409	-1067,238
Entropy J/kmol-K	-7379,148		6550,745	11688,3	18711,22	-35982,21	-2,62E+05	-2,62E+05	-4,48E+05	109,4414	-30329,24	-30329,28	-30329,28	-3,43E+05	-1,64E+05
Entropy J/kg-K	-2187,827		1870,82	3464,45	5546,065	-10665,24	-4747,284	-4747,284	-4145,206	54,28965	-14794,2	-14794,2	-14794,2	-3737,789	-9110,458
Density kmol/cum	0,043363		0,02542	0,02542	0,02542	0,258796	1,32854	17,00229	9,57759	0,04034	1,298646	1,298647	1,298646	9,463742	54,97888
Density kg/cum	0,146257		0,085737	0,089009	0,085761	0,873122	4,482206	936,8575	1035,72	0,081321	2,662327	2,662327	2,662327	867,3486	991,6043
Average MW	3,372821		3,372821	3,501536	3,373783	3,373783	3,373783	55,10185	108,1399	2,01588	2,050079	2,050077	2,050079	91,64965	18,0361
Liq Vol 60F cum/hr	58,9191	0	58,9191	57,04756	58,44702	58,44702	58,44702	1,688691	1,428108	6,408774	56,75833	51,08222	5,675833	1,442374	0,246317

Figure E.5: Stream table industrial scale, stream names/numbers corresponding to Figure E.1

E.4 Cost Estimation

The cost estimation for the BTX process is done with the same methods as in Section D.4. So, the equipment costs were estimated with the method of Towler and Sinnott [62]. The parameters for this method are shown in Table E.2.

Equipment	Detailed description	a	b	n
Vaporiser	Evaporator	88,000	65,500	0.75
Reactor	Jacketed, agitated	61,500	32,500	0.8
Compressor	Reciprocating compressor	260,000	2,700	0.75
Cooler	Packaged mechanical refrigerator evaporator	24,000	3,500	0.9
Flash column	Pressure vessel vertical	11,600	34	0.85

Table E.2: Overview of the equipment parameters [62]

Unfortunately, there are no parameters for this cost estimation method available for a decanter. This means that the costs of this equipment were estimated from other sources. In the case of the decanter, the costs were estimated to be about $30,000.00 for lab scale and $50,000.00 for industrial scale [116]. The volume of the reactor was calculated by optimising the length and diameter in the Aspen Plus^{TM} simulation environment to the best conversions. For lab scale, this resulted in a length and diameter of respectively 0.3 and 0.5 meter, giving a volume of about 0.06 m^3. However, the minimum volume for a reactor is 0.5 m^3, so this is used (as visible in Table E.3). In industrial scale, the values that resulted in the highest conversion of cresol to toluene were a length and diameter of respectively 2.5 and 0.5 meter. The diameter was thus assumed to be constant. The new industrial volume was calculated and resulted into 1.96 m^3. The other data parameters were obtained from the Aspen Plus^{TM} simulation or estimated.

Equipment	Size Unit	S lab	S industry	C_e lab	C_e industry
Vaporiser	m^2	0.5	8	$126,946.53	$399,572.26
Reactor	m^3	0.5	1.96	$80,166.35	$117,235.40
Compressor	kW	93	920	$340,858.55	$710,935.04
Cooler	kW	50	750	$142,341.58	$1,378,014.08
Flash column	kg (shell mass)	160	160	$14,140.86	$14,140.86
Decanter				$30,000.00	$50,000.00

Table E.3: Overview of the equipment costs

Table E.4 gives an overview of the fixed capital costs, calculated in the same manner as for the cost estimation of p-hydroxybenzaldehyde. The fixed operating costs are shown in Figures E.6 and E.7.

	Lab	Industry	Remarks
Total C_e	$734,454.88	$2,669,897.65	Adding all C_e equipment costs
2018 corrected	$831,206.12	$3,021,608.69	Corrected with CEPCI value of 2018 (most recent)
ISBL fixed capital costs	$3,017,278.20	$10,968,439.55	Multiply with Lang Factor (3.63)
OSBL fixed capital costs	$603,455.64	$4,387,375.82	20% of ISBL for lab scale, 40% of industrial scale
Engineering costs	$362,073.38	$1,535,581.54	10% of ISBL and OSBL
Contingency	$543,110.08	$2,303,372.30	15% of ISBL and OSBL
Total Fixed Capital Cost	$4,525,917.30	$19,194,769.21	Adding ISBL, OSBL, Engineering and Contingency

Table E.4: Overview of the costs

Chemical	Price ($/kg)	Mass flow lab (kg/year)	Mass flow industry (kg/year)	Reference
Pine Wood	0.077	48,828	143,649,440	[49], [107]
Cresol		4,000	11,766,960	
Hydrogen	1.40	656	1,713,776	[84]
NiFe				
Ni	83.33	2	200	[117]
Fe	70.00	2	200	[118]

Table E.5: Overview of the raw material costs

The remaining things are the costs of the pyrolysis process, calculated in the same manner as explained in the cost estimation for p-hydroxybenzaldehyde, and the results are shown in Figures E.6 and E.7.

Since there is no side product, the only proceeds are from the obtained toluene with a normal price of $0.80/kg and a more green price of $0.96/kg as explained in 4.2.

The previous tables are all part of the cost analysis overviews in Figures E.6 and E.7 on the following pages.

Production of toluene (BTX) from the pyrolysis of pine wood

COST OF PRODUCTION

Capital Cost Basis Year	2018
On stream	8000 hr/yr 333.33 day/yr

YIELD ESTIMATE

Yield information taken from ASPEN Pro simulation environment,
Based on theoretical values of the article published by Liu et al. (2018)

Scale of production set to lab scale: 3.4 ton/yr

Pyrolysis process costs based on data from the BTG Group

CAPITAL COSTS

	$MM
ISBL Capital Cost	3.017
OSBL Capital Cost	0.603
Engineering Costs	0.362
Contingency	0.543
Total Fixed Capital Cost	4.526
Working Capital	0.226

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Toluene	kg	1	3,399	0.8	0.003	0.80
Total Key Product Revenues (REV)	kg	1	3,399		0.003	0.80

By-products & Waste Streams	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Aqueous Waste	kg	0.193	656	-1.50	-0.000984	-0.29
Total Byproducts and Wastes (BP)	kg	0.193	656		0.00	-0.29

Raw Materials	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Pine Wood	kg	14.36391703	48,828	0.08	0.00	1.11
Hydrogen	kg	0.1929775016	656	1.40	0.0009	0.27
Total Raw Materials (RM)	kg	14.55689453	49,484		0.00	1.38
Gross Margin (GM = REV + BP - RM)					0.00	-0.87

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
NiFe						
Ni	kg	0.0006	2.00	83.33	0.0001667	0.05
Fe	kg	0.0006	2.00	70.00	0.0001400	0.04
Total Consumables (CONS)					0.00	0.09

Variable Cost of Production

		$MM/yr	$/unit product
Utilities	10% of Cash Cost of Production	0.122	35.80
Variable Cost of Production (VCOP = RM - BP + CONS + UTS)		0.12767	37.56

FIXED OPERATING COSTS

			$MM/yr	$/unit product
Labor				
	4.8 Operators per Shift Position			
Number of shift position	3	30,000 $/yr each	0.43	127.08
Supervision		25% of Operating Labor	0.11	31.77
Direct Ovhd.		45% of Labor & Superv.	0.24	71.48
Maintenance		3% of ISBL Investment	0.09	26.63
Overhead Expense				
Plant Overhead		30% of Labor & Maint.	0.26	77.09
Tax & Insurance		2% of Fixed Investment	0.07	19.97
Interest on Debt Financing		0% of Fixed Capital	0.00	0.00
		6% of Working Capital	0.01	3.99
Fixed Cost of Production (FCOP)			1.22	358.02

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	4.526	15%	15	0.171	0.77	227.69
Total Annual Capital Charge					0.77	227.69

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	0.1277	37.56
Fixed Cost of Production	1.22	358.02
Cash Cost of Production	1.34	395.58
Pyrolysis Process Production Costs	0.0087	2.57
Gross Profit	-1.35	-397.35
Total Cost of Production	2.13	625.84

Figure E.6: Economic Analysis of BTX production (small scale)

Production of toluene (BTX) from the pyrolysis of pine wood

COST OF PRODUCTION

Capital Cost Basis Year	2018
On stream	8000 hr/yr 333.33 day/yr

YIELD ESTIMATE		CAPITAL COSTS	
			$MM
Yield information taken from ASPEN Pro simulation environment,		ISBL Capital Cost	10.968
Based on theoretical values of the article published by Liu et al. (2018)		OSBL Capital Cost	4.387
		Engineering Costs	1.536
Scale of production set to lab scale: 10 kton/yr		Contingency	2.303
		Total Fixed Capital Cost	19.195
Pyrolysis process costs based on data from the BTG Group		Working Capital	0.960

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Toluene	kg	1	10,004,160	0.8	8.003	0.80
Total Key Product Revenues (REV)	kg	1	10,004,160		8.003	0.80
By-products & Waste Streams						
Aqueous Waste	kg	0.194	1,936,480	-1.50	-2.90	-0.29
Total Byproducts and Wastes (BP)	kg	0.194	1,936,480		-2.90	-0.29
Raw Materials						
Pine Wood	kg	14.35897067	143,649,440	0.08	11.06	1.11
Hydrogen	kg	0.1713063366	1,713,776	1.40	2.40	0.24
Total Raw Materials (RM)	kg	14.530277	145,363,216		13.46	1.35
				Gross Margin (GM = REV + BP - RM)	-8.36	-0.84

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
NiFe						
Ni	kg	0.0000	200.00	83.33	0.0166660	0.00
Fe	kg	0.0000	200.00	70.00	0.0140000	0.00
Total Consumables (CONS)					0.03	0.00

Variable Cost of Production

		$MM/yr	$/unit product
Utilities	10% of Cash Cost of Production	1.679	0.168
	Variable Cost of Production (VCOP = RM - BP + CONS + UTS)	18.075	1.81

FIXED OPERATING COSTS

				$MM/yr	$/unit product
Labor					
	4.8 Operators per Shift Position				
Number of shift position	3		30,000 $/yr each	0.43	0.04
Supervision			25% of Operating Labor	0.11	0.01
Direct Ovhd.			45% of Labor & Superv.	0.24	0.02
Maintenance			3% of ISBL Investment	0.33	0.03
Overhead Expense					
Plant Overhead			30% of Labor & Maint.	0.33	0.03
Tax & Insurance			2% of Fixed Investment	0.29	0.03
Interest on Debt Financing			0% of Fixed Capital	0.00	0.00
			6% of Working Capital	0.06	0.01
			Fixed Cost of Production (FCOP)	1.79	0.18

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	19.195	15%	15	0.171	3.28	0.33
				Total Annual Capital Charge	3.28	0.33

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	18.07	1.81
Fixed Cost of Production	1.79	0.18
Cash Cost of Production	19.87	1.99
Pyrolysis Process Production Costs	25.72	2.57
Gross Profit	-37.59	-3.76
Total Cost of Production	48.87	4.89

Figure E.7: Economic Analysis of BTX production (industrial scale)

Production of toluene (BTX)

COST OF PRODUCTION

Capital Cost Basis Year	2018
On stream	8000 hr/yr 333.33 day/yr

YIELD ESTIMATE

Yield information taken from ASPEN Pro simulation environment,
Based on theoretical values of the article published by Liu et al. (2018)

Scale of production set to lab scale: 10 kton/yr

Pyrolysis process costs based on data from the BTG Group

CAPITAL COSTS

	$MM
ISBL Capital Cost	10.968
OSBL Capital Cost	4.387
Engineering Costs	1.536
Contingency	2.303
Total Fixed Capital Cost	19.195
Working Capital	0.960

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Toluene	kg	1	10,004,160	1.0	9.604	0.96
Total Key Product Revenues (REV)	kg	1	10,004,160		9.604	0.96

By-products & Waste Streams						
Aqueous Waste	kg	0.194	1,936,480	-1.50	-2.90	-0.29
Total Byproducts and Wastes (BP)	kg	0.194	1,936,480		-2.90	-0.29

Raw Materials						
Pine Wood	kg	14.35897067	143,649,440	0.08	11.06	1.11
Hydrogen	kg	0.1713063366	1,713,776	1.40	2.40	0.24
Total Raw Materials (RM)	kg	14.530277	145,363,216		13.46	1.35

				Gross Margin (GM = REV + BP - RM)	-6.76	-0.68

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
NiFe						
Ni	kg	0.0000	200.00	83.33	0.0166660	0.00
Fe	kg	0.0000	200.00	70.00	0.0140000	0.00
Total Consumables (CONS)					0.03	0.00

Variable Cost of Production

				$MM/yr	$/unit product
Utilities	10% of Cash Cost of Production			1.679	0.168
	Variable Cost of Production (VCOP = RM - BP + CONS + UTS)			18.075	1.81

FIXED OPERATING COSTS

				$MM/yr	$/unit product
Labor					
	4.8 Operators per Shift Position				
Number of shift position	3		30,000 $/yr each	0.43	0.04
Supervision			25% of Operating Labor	0.11	0.01
Direct Ovhd.			45% of Labor & Superv.	0.24	0.02
Maintenance			3% of ISBL Investment	0.33	0.03
Overhead Expense					
Plant Overhead			30% of Labor & Maint.	0.33	0.03
Tax & Insurance			2% of Fixed Investment	0.29	0.03
Interest on Debt Financing			0% of Fixed Capital	0.00	0.00
			6% of Working Capital	0.06	0.01
			Fixed Cost of Production (FCOP)	1.79	0.18

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	19.195	15%	15	0.171	3.28	0.33
				Total Annual Capital Charge	3.28	0.33

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	18.07	1.81
Fixed Cost of Production	1.79	0.18
Cash Cost of Production	19.87	1.99
Pyrolysis Process Production Costs	25.72	2.57
Gross Profit	-35.99	-3.60
Total Cost of Production	48.87	4.89

Figure E.8: Economic Analysis of BTX production (green price)

Production of toluene (BTX)

COST OF PRODUCTION

Capital Cost Basis Year   2018
On stream   8000 hr/yr   333.33 day/yr

YIELD ESTIMATE | CAPITAL COSTS

Yield information taken from ASPEN Pro simulation environment,	
Based on theoretical values of the article published by Liu et al. (2018)	

	$MM
ISBL Capital Cost	10.968
OSBL Capital Cost	4.387
Engineering Costs	1.536
Scale of production set to lab scale: 10 kton/yr	Contingency	2.303
	Total Fixed Capital Cost	19.195
Pyrolysis process costs based on data from the BTG Group	Working Capital	0.960

REVENUES AND RAW MATERIAL COSTS

Key Products	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit main product
Toluene	kg	1	10,004,160	4.6	46.019	4.60
Total Key Product Revenues (REV)	kg	1	10,004,160		46.019	4.60

By-products & Waste Streams						
Aqueous Waste	kg	0.194	1,936,480	-1.50	-2.90	-0.29
Total Byproducts and Wastes (BP)	kg	0.194	1,936,480		-2.90	-0.29

Raw Materials						
Pine Wood	kg	14.35897067	143,649,440	0.08	11.06	1.11
Hydrogen	kg	0.1713063366	1,713,776	1.40	2.40	0.24
Total Raw Materials (RM)	kg	14.530277	145,363,216		13.46	1.35
				Gross Margin (GM = REV + BP - RM)	29.65	2.96

CONSUMABLES

	Units	Units/Unit product	Units/yr	Price $/unit	$MM/yr	$/unit product
NiFe						
Ni	kg	0.0000	200.00	83.33	0.0166660	0.00
Fe	kg	0.0000	200.00	70.00	0.0140000	0.00
Total Consumables (CONS)					0.03	0.00

Variable Cost of Production

		$MM/yr	$/unit product
Utilities	10% of Cash Cost of Production	1.679	0.168
	Variable Cost of Production (VCOP = RM - BP + CONS + UTS)	18.075	1.81

FIXED OPERATING COSTS

			$MM/yr	$/unit product
Labor				
4.8 Operators per Shift Position				
Number of shift position	3	30,000 $/yr each	0.43	0.04
Supervision		25% of Operating Labor	0.11	0.01
Direct Ovhd.		45% of Labor & Superv.	0.24	0.02
Maintenance		3% of ISBL Investment	0.33	0.03
Overhead Expense				
Plant Overhead		30% of Labor & Maint.	0.33	0.03
Tax & Insurance		2% of Fixed Investment	0.29	0.03
Interest on Debt Financing		0% of Fixed Capital	0.00	0.00
		6% of Working Capital	0.06	0.01
		Fixed Cost of Production (FCOP)	1.79	0.18

ANNUALIZED CAPITAL CHARGES

	$MM	Interest Rate	Life (yr)	ACCR	$MM/yr	$/unit product
Fixed Capital Investment	19.195	15%	15	0.171	3.28	0.33
				Total Annual Capital Charge	3.28	0.33

SUMMARY

	$MM/yr	$/unit product
Variable Cost of Production	18.07	1.81
Fixed Cost of Production	1.79	0.18
Cash Cost of Production	19.87	1.99
Pyrolysis Process Production Costs	25.72	2.57
Gross Profit	0.43	0.04
Total Cost of Production	48.87	4.89

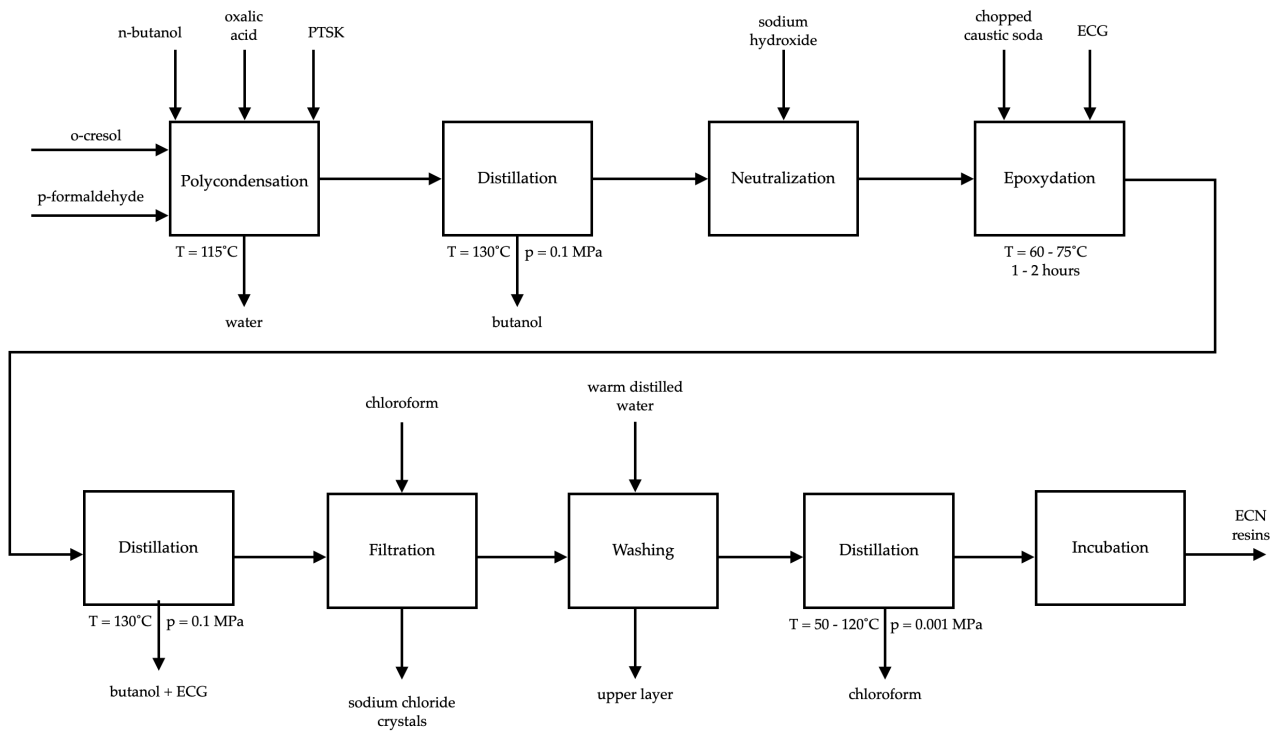**Figure E.9: Economic Analysis of BTX production (trial and error)**

F ECN resins extended block diagram

Figure F.1: Block diagram of ECN resin production