

Lignin depolymerisation to phenol with supercritical water as a medium

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Abstract

In this bachelor assignment the feasibility of phenol production from lignin depolymerisation with supercritical water is determined. 850kg of phenol is produced per hour from 20 tonnes of lignin which is the amount of available lignin in the Kvarnsveden paper mill in Sweden. A model is made where phenol is produced and purified from lignin, the lignin is normally used as fuel in paper mills and provides about 40% of the energy to the paper process. 179GJ/tonne phenol or 42.2 MW is needed to fill the energy gap of the paper and phenol process. Coal worth €570 is needed to fill this energy gap, a tonne of phenol is worth about €1225, since the main costs are the energy costs it can be said that the process can be feasible and there still is potential for improvement with other substances produced in the process.

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Introduction

Lignin is one of the main substances in wood, 20 to 30wt.% of wood consists of lignin, depending on the sort of wood.[1] The paper industry produces all kinds of paper and cardboard products. In paper the lignin share has to be as low as possible, so the lignin is separated from the cellulose, which produces the pulp of which the paper is produced. The lignin is used by burning it as a fuel to provide energy to the process as shown in figure 1.

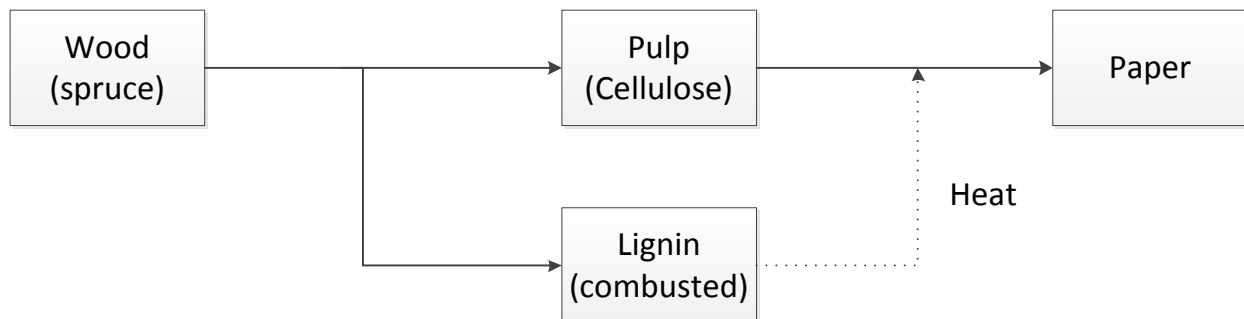


Fig 1. Concept of the use of lignin in the paper process

Lignin molecules are large molecules with a large amount of aromatic rings, the molecular weight ranges between 260 and 50 million g/mol.[2] An example of how lignin looks is shown in figure 2.

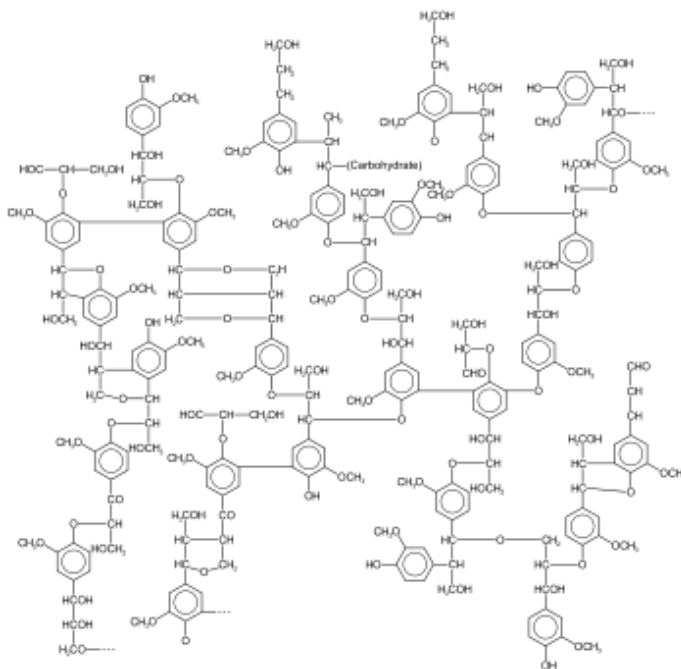


Fig 2. An illustration of lignin which shows there are many aromatic bindings

The purpose of this bachelor assignment is to see if a process can be build where the lignin is converted to a substance (in this case phenol), this way an usable substance could be produced out of lignin instead of just using it as fuel.

There are many different ways to depolymerize lignin: catalytic conversion, which can be divided in hydro treatment, oxidative, enzymatic and cracking. Then there also are pyrolysis and solvolysis.[3] In this bachelor assignment the depolymerisation of lignin will be done with supercritical water. Water becomes supercritical at a temperature of 374.2°C and at a pressure of 22.12MPa. The big advantage of supercritical fluids is that the solubility can be controlled by changing the temperature and pressure; the temperature and pressure can be adjusted to make the properties of the water more liquid- or gas-like.

The goal is to create a concept as shown in figure 3. Where the lignin is converted to phenol and the remaining substances are burned as fuel.

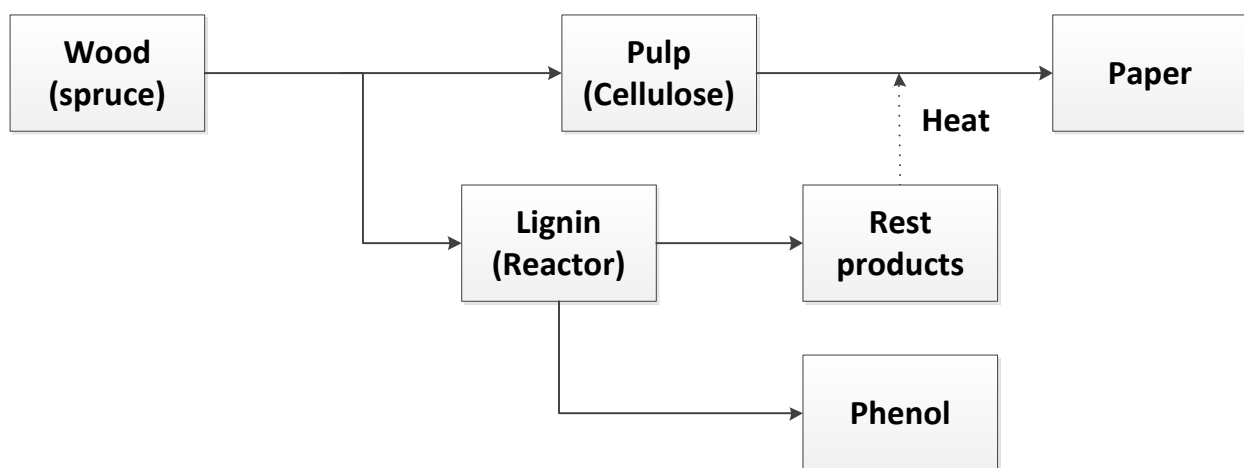


Fig 3. Simplification of the paper process of what could be done in the future

To get an indication of how the process could work in reality a model is made of the production and purification of phenol from lignin. The model is build in Aspen Plus modeling, this is a modeling program mainly used by engineers, it's used for conceptual design and optimization of chemical processes.

In the paper industry vast amounts of raw materials is needed to produce paper, every day 1973 tonnes of paper are produced at the Kvarnsveden mill. The materials used are 3800 m³ wood, 87 800 m³ water, 100 tonnes pulp, 186 tonnes of process chemicals and 148 tonnes of filler.[4]

In table 1 the energy released by burning lignin is shown.

wood consumption	3800 [4]	m ³ /day
density spruce	450 [5]	kg/m ³
share lignin in spruce	27 [6]	wt%
energy content	25500 [7]	kJ/kg
Total energy	11.8	TJ/day
Total energy	136300	kW

Table 1. Energy from the lignin burned in the paper mill, spruce is mostly used in the Kvarnsveden paper mill [8]

Almost 11.8 TJ/day of energy could be produced. The energy used in this 24 hours to produce 1973 tonnes of paper is 27.5 TJ/day (appendix A and B). So the share of energy produced by the lignin could provide 43 percent of the total energy needed in the paper mill.

The energy of rest products that will be burned to provide energy to the process will be less than the energy that could be provided by the lignin. This energy gap plus the energy needed for the phenol production process will be the total energy needed for the production of phenol. The amount of produced phenol than has to be compared with the costs of the process, which mostly is the energy needed for the process.

The research question then becomes:

Is it feasible to produce phenol from lignin with supercritical water instead of burning the lignin as a fuel?

In Figure 4. the process flow diagram of the process is shown. Lignin is loaded in V101 and then transported to the reactor (R101) when the valve is opened. The system contains three reactors, since the process starts as a batch process (in greater detail further on). The process has to be done in batches because lignin consists of large solids and cannot be transported through pumps. Then water is pumped into the reactor from storage tank T101 and heated. The reactor is heated to 400°C and the reactor runs for about 4 hours. Then the products are transported through heat exchanger H101 to storage tank T102 and a continues process begins after the tank. First water and carbon monoxide are flash off in V102, and streams back to T102. The other stream is mixed with MIBK and the water is separated in V103. In V104 the largest share of the MIBK is separated to the top stream and the remaining organic components get to V105. In column V105 to V108 phenol is separated from the remaining rest products in four steps. The process contains more valves, but these could not be shown clearly in the process flow diagram.

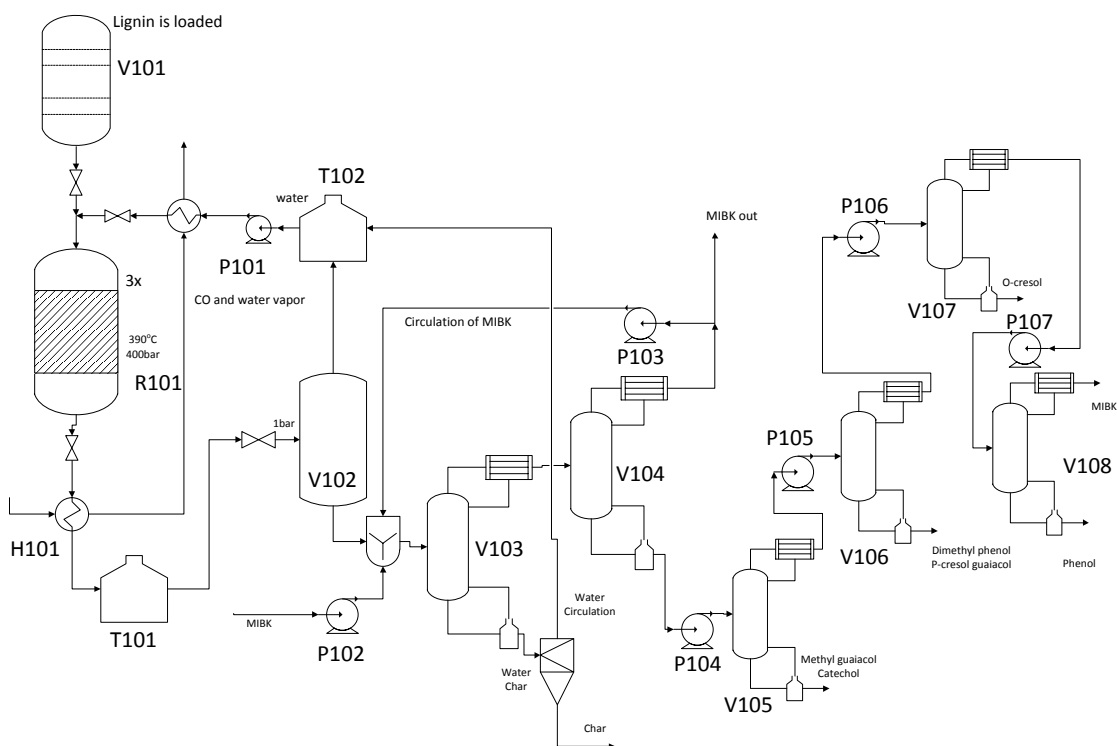


Fig.4 Process flow diagram of the process.

Theory

Chemistry

Hydrothermal decomposition of alkali lignin in sub- and supercritical water by *Piñkowska et al.*[9] is the paper which the chemical part of this bachelor assignment is based on.

The molecular weight for the lignin used in the project is 28000g/mol. The lignin used contained 61.31mol% carbon, 5.35mol% hydrogen, 31.47mol% oxygen, 0.49 mol% nitrogen and 1.38mol% sulfur. Together this led to the formula for the lignin; $C_{1430}H_{1497}O_{552}N_{11}S_{11}$. The formula for lignin was unfortunately too big for Aspen to handle the formula has been changed for simplification, nitrogen and sulfur have been taken out of the formula and since $C_{1430}H_{1497}O_{552}$ still was too large to fit in the formula has been divided by two which gives; $C_{715}H_{748}O_{226}$. It is good to keep in mind that the actual lignin is twice as large than the input for Aspen. The lignin (input Aspen) has a molecular weight of 12957 g/mol.

To get the highest possible yield of phenol the residence time in the reactor have been set to 4 hours. The graph is shown here below: The phenol yield becomes higher the longer the process is going on.

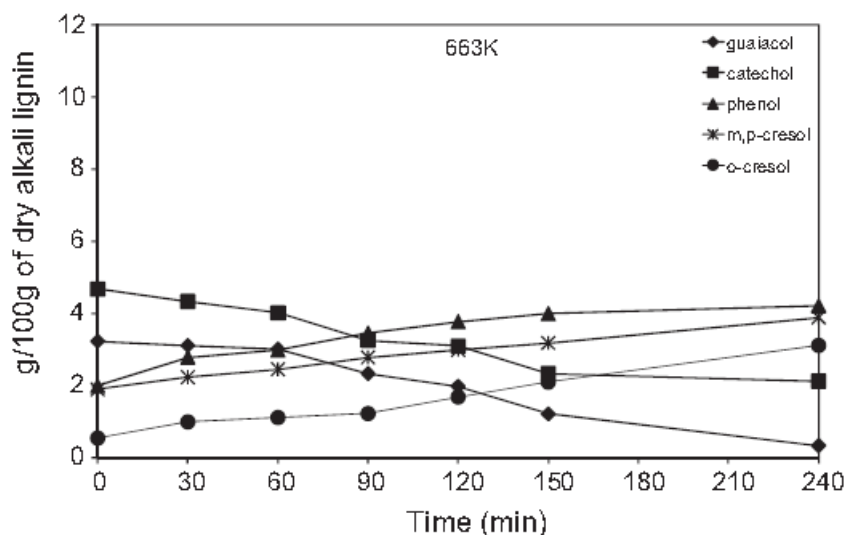


Figure 3. The yield of products depends on the time spent in the reactor at 390°C. [9]

The most important substances produced in the process are shown in figure 4. These substances are all very much like phenol. The main difference is the fact that these substances have some extra hydroxy, methyl or methoxy group(s), the other substances not mentioned here also have these extra groups, and are have slightly higher molecular weights than the substances shown.

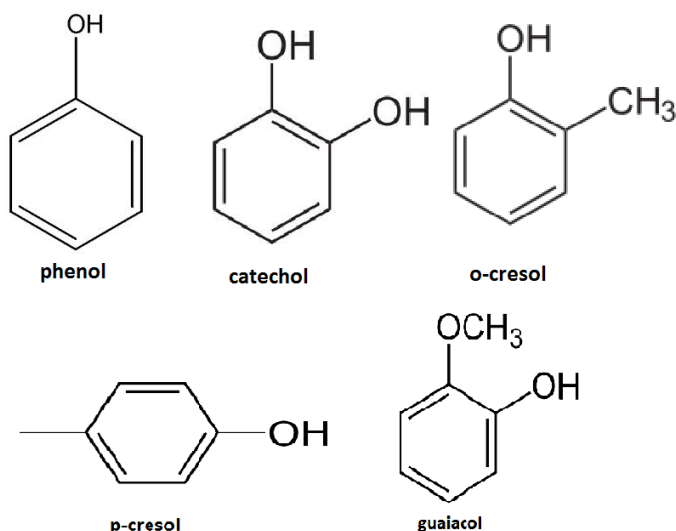


Fig. 4. Most important products produced in the process.

In the paper a methanol insoluble part was separated from the soluble part, the share of insoluble is shown in the graph:

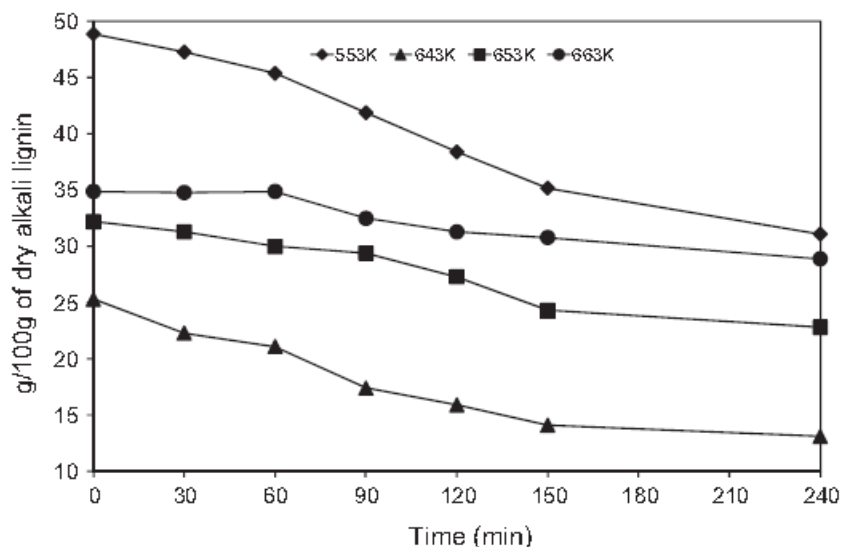


Fig 5. Methanol insoluble part of the lignin, which depends on the residence time [9]

The residue substance which later in the experiment was insoluble in a methanol/water mixture. As shown in figure 3. The methanol insoluble part is taken to be 28mol% for 390°C or 663K after 240 minutes. Together with the empirical formula for the residue substance ($C_{10}H_{1.86}O_{0.56}N_{0.05}S_{0.07}$) this gives a formula of $C_{280}H_{52}O_{16}$. This residue contains many different hydrocarbons which were not identified, this part will be burned as a fuel, so it does not matter which molecules are in there. Assumed is that $C_{280}H_{52}O_{16}$ will just be burned like the lignin was before. At 563K or 390°C the products created are shown in appendix A. Not all substances were used for input in Aspen. Important substances like phenol, o-cresol, p-cresol, catechol and guaiacol have been put in normally. The two larger substances; methyl-guaiacol and dimethyl phenol which are not directly interesting for the study have also the remaining share substances in them. It is assumed that these substances will all be burned and this way they do not change the share of phenol, catechol, cresol and guaiacol. (For the full component list see appendix C) With all this information the reaction formula was calculated in Excel and is shown in table 2.

<i>input</i>	
Lignin	100
<i>output</i>	
Phenol	613
Catechol	612
P-Cresol	468
O-Cresol	319
Guaiacol	710
Methyl Guaiacol	1300
Dimethyl Phenol	1118
Char	6136
CO	191
H₂O	13047
Residue	100

Table 2. the reaction formula in table form

The reactor input in the experiment is 5% lignin and 95% water. In the model the amounts of lignin and water have been assumed to be both 20000 kg/h. An assumption is made that all the lignin will dissolve with this amount of water. In the real process the water will be used as many times as possible and it will not matter if more water has to be used, the amount of water mostly matters for the reactor size.

Technology

The Reactors

The reactors have to be vessels which can cope with high pressure, the pressure in the vessel will be 400 bar. Since the residence time in the reactor is 4 hours and 20 tonnes of lignin is available per hour. One reactor should be able to contain 80 tonnes of lignin and 80 tonnes of water.

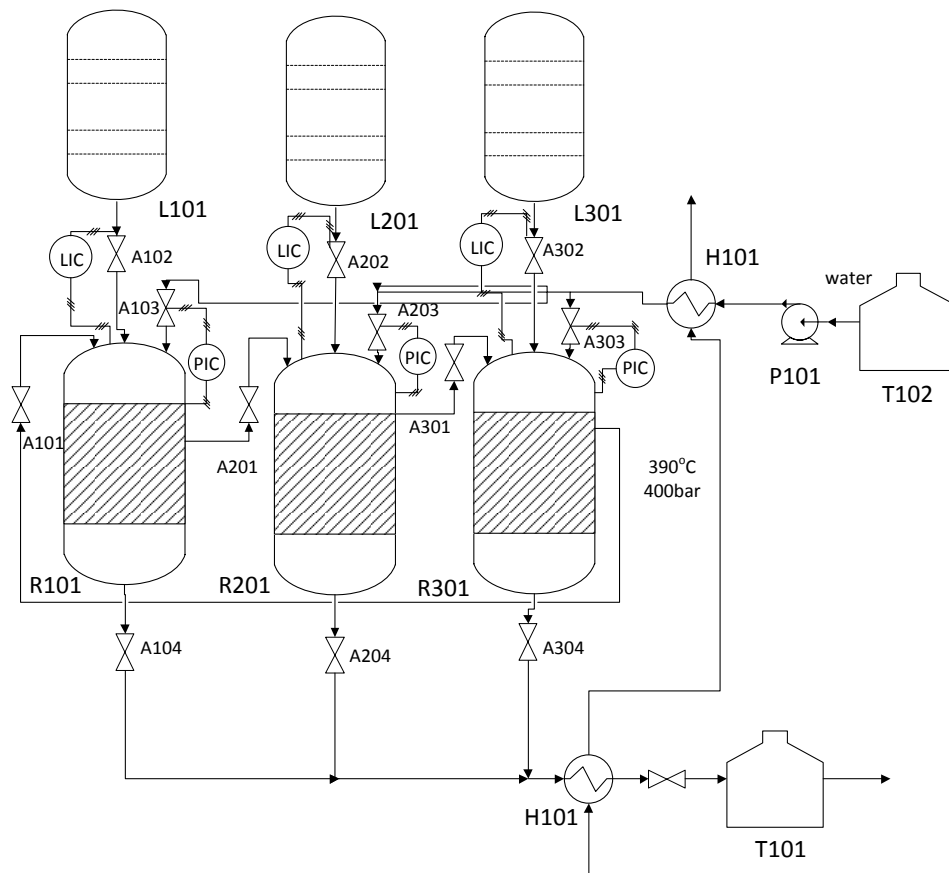


fig 6. P&ID of the reactors

The reactors are shown in figure 6. First valve A102 opens so the lignin falls into the reactor R101, then valve A101 opens and water from the third reactor R301 flows in the first reactor and the pressure in reactor R101 increases, then more water is pumped into the reactor from storage tank T102 to get the pressure to 400bar, this stream is already heated by heat exchanger H101, but a coil heats the reactor until 390°C is reached. After 4 hours when the reaction is finished valve A103 opens and the water is partly flashed to Reactor R201, after that valve A104 opens and the products with the water stream into storage tank T101, after T101 the process runs continuously. Valve A102, A202 and A302 are connected to a level indicator controller to control the amount of lignin entering the reactor. Valve A103, A203 and A303 are connected to a pressure indicator to controller to get the reactors to 400 bar. The remaining valves have to be opened and closed depending on the time, if the reactor is getting filled, closed or emptied.

Distillation columns

Several Distillation columns are used in the process, because there will be many different compounds which have to be separated from the phenol to make the phenol usable as a chemical in industry. The height of these columns will vary from 8 to 12 meters depending on the number of stages which is 40 to 60 stages. reflux ratios, vary from 2 to 10 in the different distillation columns.

Solid handling pumps

Some solid handling pumps will have to be used in the process. Char will be formed in the reactors, so the pumps after the reactors should be able to cope with char particles.



fig 7. Distillation column as will be used in the process

Results

The Model

The most important information from the model are shown in these results.

The components used as input for the model are shown in table 3. Methyl guaiacol, lignin and residue were put in the model under user defined, methyl guaiacol was added with input draw structure.

Component ID	Type	Component name	Formula
PHENOL	CONV	PHENOL	C6H6O
CATECHOL	CONV	1,2-BENZENEDIOL	C6H6O2-E1
GUAIACOL	CONV	GUAIACOL	C7H8O2-E1
O-CRESOL	CONV	O-CRESOL	C7H8O-3
P-CRESOL	CONV	P-CRESOL	C7H8O-5
DIMEPHNL	CONV	2,6-XYLENOL	C8H10O-8
MEGUAIAIC	CONV	ETHYLBENZENE-HYDROPEROXIDE	C8H10O2
CHAR	SOLID	CARBON-GRAPHITE	C
CO	CONV	CARBON-MONOXIDE	CO
H2O	CONV	WATER	H2O
LIGNIN	CONV		C715H748O226
RESIDUE	CONV		C280H52O16
MIBK	CONV	METHYL-ISOBUTYL-KETONE	C6H12O-2

Component	Input
1.1	1.1.1
1.2	1.2.1
1.3	1.3.1
1.4	1.4.1
1.5	1.5.1
1.6	1.6.1
1.7	1.7.1
1.8	1.8.1
1.9	1.9.1
1.10	1.10.1
1.11	1.11.1
1.12	1.12.1
1.13	1.13.1
1.14	1.14.1
1.15	1.15.1
1.16	1.16.1
1.17	1.17.1
1.18	1.18.1
1.19	1.19.1
1.20	1.20.1
1.21	1.21.1
1.22	1.22.1
1.23	1.23.1
1.24	1.24.1
1.25	1.25.1
1.26	1.26.1
1.27	1.27.1
1.28	1.28.1
1.29	1.29.1
1.30	1.30.1
1.31	1.31.1
1.32	1.32.1
1.33	1.33.1
1.34	1.34.1
1.35	1.35.1
1.36	1.36.1
1.37	1.37.1
1.38	1.38.1
1.39	1.39.1
1.40	1.40.1
1.41	1.41.1
1.42	1.42.1
1.43	1.43.1
1.44	1.44.1
1.45	1.45.1
1.46	1.46.1
1.47	1.47.1
1.48	1.48.1
1.49	1.49.1
1.50	1.50.1
1.51	1.51.1
1.52	1.52.1
1.53	1.53.1
1.54	1.54.1
1.55	1.55.1
1.56	1.56.1
1.57	1.57.1
1.58	1.58.1
1.59	1.59.1
1.60	1.60.1
1.61	1.61.1
1.62	1.62.1
1.63	1.63.1
1.64	1.64.1
1.65	1.65.1
1.66	1.66.1
1.67	1.67.1
1.68	1.68.1
1.69	1.69.1
1.70	1.70.1
1.71	1.71.1
1.72	1.72.1
1.73	1.73.1
1.74	1.74.1
1.75	1.75.1
1.76	1.76.1
1.77	1.77.1
1.78	1.78.1
1.79	1.79.1
1.80	1.80.1
1.81	1.81.1
1.82	1.82.1
1.83	1.83.1
1.84	1.84.1
1.85	1.85.1
1.86	1.86.1
1.87	1.87.1
1.88	1.88.1
1.89	1.89.1
1.90	1.90.1
1.91	1.91.1
1.92	1.92.1
1.93	1.93.1
1.94	1.94.1
1.95	1.95.1
1.96	1.96.1
1.97	1.97.1
1.98	1.98.1
1.99	1.99.1
1.100	1.100.1

Figure 8 shows an the whole process, which is explained step by step further on.

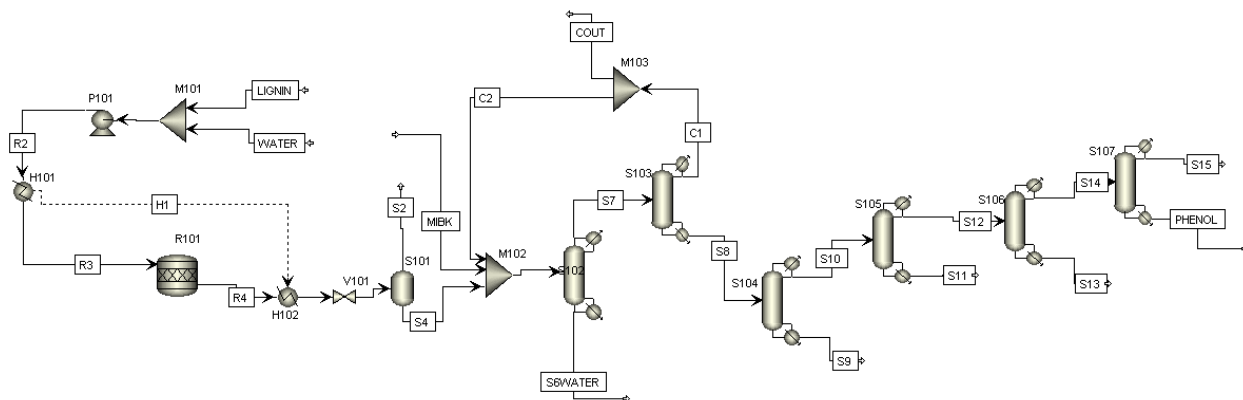


Fig 8. Overview of the model

Figure 9. shows the reaction part of the process. Water is added to the lignin, the stream is then heated and pressurized and flows into the reactor where the reaction takes place, after the reactor the heat is partly recovered by a second heat exchanger, which is connected to the first heat exchanger.

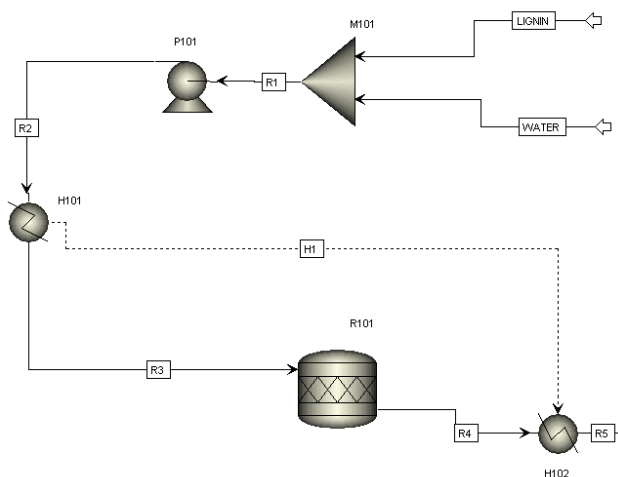


Fig 9. Reaction part of the process

Figure 10 shows the different components with their coefficients, the reaction takes place under a temperature of 390°C and pressure of 400 bar.

Reaction No.: ☒ 1

Reactants	Component	Coefficient
	LIGNIN	-100
	*	

Products	Component	Coefficient
	PHENOL	613
	CATECHOL	612
	P-CRESOL	468
	O-CRESOL	319
	GUAIACOL	710
	MEGUAIAIC	1300
	DIMEPHNL	1118
	CHAR	6136
	CO	191
	H2O	13047
	RESIDUE	100

Products generation

☐ Molar extent: kmol/hr

☒ Fractional conversion: of component

Fig. 10. Reaction formula input

The purification part of the process is where the phenol is purified, the first stages are shown in figure 11. It starts at the first valve (V101) where the pressure drops down to 1atm. The the largest part of the CO leaves the system in the separator S101 which flashes at 80°C. Then MIBK (Methyl isobutyl ketone) is added with a capacity of 10000kg/h. This has to be done to get the phenol in the organic phase, because normal distillation of water and phenol leads to a huge loss of phenol yield, since phenol is soluble in water. After addition of MIBK the largest part of the water is separated in S102 (sep2 block) and the other stream continues into S103 where the main part of the MIBK streams out in the top stream so it can circulate back into the system. The phenol and other organic components continue in stream S8 out of separation block S103.

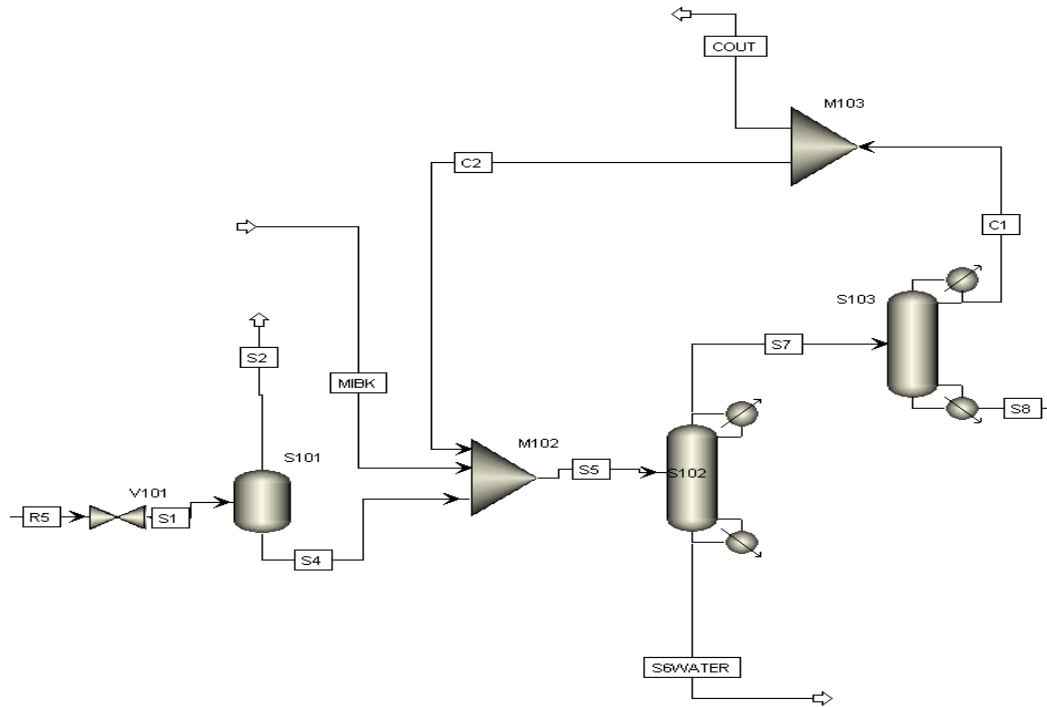


Fig.11. separation of phenol (part 1)

The Sep2 block (S102) has been defined as shown in table 4. An assumption is made here that 99,8% of the water is separated from the phenol stream here. 2% of the organic components follow with the water stream. Phenol is most important to mention here, phenol that is lost here lowers the phenol yield, the other components would just be separated further on in the system. It is also assumed that the char is flows out with the water in the bottom stream (s6 water).

Component ID	split fraction (S6 water)
PHENOL	0.02
CATECHOL	0.02
GUAIACOL	0.02
O-CRESOL	0.02
P-CRESOL	0.02
DIMEPHNL	0.02
MEGUAIAIC	0.02
CHAR	1
CO	0
H2O	0.998
LIGNIN	0
RESIDUE	0
MIBK	0.01

table 4. the bottom stream with defined split fractions.

The specification of the S103 column is shown in table 5, in table 6 the streams out of S103 are shown, the topstream 8(C1) contains most of the MIBK, the water and CO remaining in the stream stream out of the top as well. The bottom stream (S8) contains all the organic component, also a small share of the MIBK flows out here.

specification	S103
number of stages	40
feedstage	20
reflux ratio	6
distillate to feed ratio	0.6

table 5. input of distillation column S103

Mass Flow kg/hr	C1	S8
PHENOL	0	872
CATECHOL	0	1019
GUAIACOL	0	1333
O-CRESOL	0	522
P-CRESOL	0	765
DIMEPHNL	0	2066
MEGUAIAIC	0	2717
CO	26	0
H2O	47	0
RESIDUE	0	5666
MIBK	12201	429

table 6. the streams out of S103

In the second part of the purification part the phenol has to be separated from the organic compounds, in Aspen this is done with 4 radfrac distillation columns shown in figure 12. The phenol streams through S10, S12, S14 and finally into the phenol outstream. The first three times the phenol flows out of the topstream of the columns, because phenol is the lightkey except in the last column where the remaining MIBK is separated from the phenol.

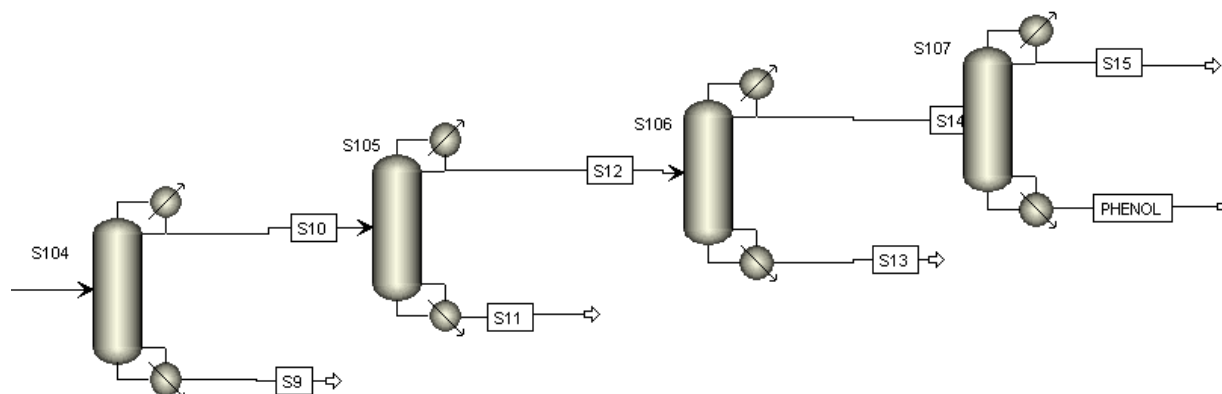


Fig 12. separation of phenol (part 2)

Table 7. shows how the different radfrac distillation columns are specified in the model. It is noticeable that column S106 has a very high reflux ratio and distillate to feed ratio, this is because the separation of phenol and O-cresol is difficult, if these ratios are less, a large share of the phenol will follow out with the O-cresol stream.

specification	S104	S105	S106	S107
number of stages	40	40	60	50
Feed stage	20	20	32	25
reflux ratio	2	5	10	5
distillate to feed ratio	0.5	0.4	0.8	0.32

Table 7. Aspen input for the four separation columns.

Table 8 and 9 show the mass fraction and mass flow of the streams where the phenol flows through, the streams are shown in figure 9.

Mass Fraction	S8	S10	S12	S14	phenol
PHENOL	0.057	0.189	0.526	0.663	0.994
CATECHOL	0.066	0.000	0.000	0.000	0.000
GUAIACOL	0.087	0.139	0.000	0.000	0.000
O-CRESOL	0.034	0.113	0.211	0.004	0.005
P-CRESOL	0.050	0.122	0.000	0.000	0.000
DIMEPHNL	0.134	0.344	0.003	0.000	0.000
MEGUAIAIC	0.177	0.000	0.000	0.000	0.000
RESIDUE	0.368	0.000	0.000	0.000	0.000
MIBK	0.028	0.093	0.261	0.334	0.000

Table 8. the mass fraction of streams with phenol in it

Mass Flow kg/hr	S8	S10	S12	S14	phenol
PHENOL	872.3	872.3	864.8	851.6	851.6
CATECHOL	1019.4	0.0	0.0	0.0	0.0
GUAIACOL	1333.2	644.0	0.2	0.0	0.0
O-CRESOL	521.7	520.1	346.5	4.7	4.7
P-CRESOL	765.4	565.8	0.2	0.0	0.0
DIMEPHNL	2066.0	1589.0	4.6	0.0	0.0
MEGUAIAIC	2716.9	0.0	0.0	0.0	0.0
RESIDUE	5666.4	0.0	0.0	0.0	0.0
MIBK	428.6	428.6	428.6	428.6	0.1

Table 9. shows the mass flow of streams with phenol in it

stream S8 streams into the first column (S104) shown in figure 9. S10 is the top stream out of S104 and in the tables it can be seen that in the first column catechol, methyl guaiacol and the residue components are separated from the phenol stream. The top stream (S12) is the phenol stream out of the second column (S105), guaiacol, P-cresol and most of the dimethyl phenol are no longer in S12 and have been separated in the second column. After the second column only O-cresol, MIBK and small amount of P-cresol and dimethyl phenol are still part of the phenol stream. After S106 in stream S14 the O-cresol is almost completely gone and only MIBK needs to be separated from the phenol. This happens in S107 where the phenol exits in the bottom stream since MIBK is the light key here.

Energy calculations

Phenol specifications:

Phenol as any chemical should have a certain purity for usage in the industry. The purity of phenol should be 99.0-99.5%. [11]

In the modeled process the produced phenol has a purity of 99.4%, which means that the phenol is up to standards. Where the polluting component is mostly O-cresol which is very similar to phenol.

Production:

In the process 850 kg/h phenol is produced, So $850/20000 = 4.25$ wt.% phenol is usable phenol from lignin after the final separation stage.

Energy use of the system:

The energy use of the reaction part is 2800 kW or 11.9 GJ/tonne phenol (appendix D). In the purification part an assumption is made that for the distillation columns 80% of the energy from the heat exchangers of the condensor is usable for as energy input for the boiler. With this information the energy use for the second stage becomes 4700 kW or 19.9 GJ/tonne phenol (appendix D). Together 7500 kW or 31.8 GJ/tonne phenol of energy is necessary for the phenol production process.

Energy gap:

The streams s9, s11 and s13 (fig. 12) can all be burned to provide energy. The calculations from these streams can be found in Appendix E. These stream together can provide 453 GJ/tonne phenol (107MW). The energy that could have been provided by burning the lignin would have been 600 GJ/tonne phenol (142MW), this means there is a certain energy gap which has to be filled up by other energy sources. the energy gap is 147 GJ/tonne phenol (34.7MW).

The total energy needed to produce for the production of a tonne of phenol is 7.5 MW from the phenol production process and 34.7MW from the energy gap of in the paper process, so the total is 42.2 MW.

The price of coal was €3.22/GJ in 2011.[12] The energy needed for both process is 179 GJ to produce one tonne of phenol. With this coal price the financial costs would be €576 per produced tonne phenol. The market price of a tonne phenol is about 1250 euro. [13]

Discussion

The Kvarnsveden papermill in Borlänge, Sweden produces 1973 tonnes of paper per day. To produce this amount of paper 3800m³ of wood is used every day. From this wood 20 tonnes of lignin is available for use every hour. Burning the lignin like it is burned in the conventional paper process now supplies 600 GJ/tonne phenol (142MW). If instead phenol would be produced in the new phenol process then 20 tonnes of lignin gives 850 kg of phenol per hour with a purity of 99.4%. The remaining substances produced in the reactor are combusted like the lignin is in the paper process which gives 453 GJ/tonne phenol (107MW). So there is a energy gap of 147 GJ/tonne phenol (34.7MW) for the paper process, this energy together with the energy of the phenol process 31.8 GJ/tonne phenol (7.5 MW) is the energy needed to produce phenol which is 179 GJ/tonne phenol (42.2 MW).

It is assumed that the energy costs are by far the greatest financial costs in the process. For the phenol process methyl isobutyl ketone is needed to separate the phenol from the water, MIBK is a chemical with a price of about €1600 per tonne. Assumed is that very little MIBK needs to be added to the process and the costs of MIBK are therefore negligible, this is because the MIBK keeps circulating through the system. Equipment costs are also part a process of course, but this not determined and assumed to be a lot smaller than the energy costs for the system and there negligible to see if the process is feasible.

So the energy costs are the main costs of the system, by determining these we can at least say if the process would be feasible or not. The total energy gap of 179 GJ/tonne phenol (42.2 MW) would cost about €575 per tonne phenol, if fueled with coal. Compared to the price that phenol is sold on the market which is €1225 per tonne phenol we can state that this process could be feasible, since the phenol sells for a price which is more than twice the price energy would cost with coal.

The process could be even more profitable if the substances like, O-cresol, P-cresol and catechol maybe even more substances could be sold on the market instead of burning them. They would have to be separated and purified, the energy costs would only increase a few procent on top of the 31.8 GJ/tonne phenol (7.5 MW) from the phenol process, but the profits would probably rise tremendously. If the market is not large enough to sell these substances a process could possibly be added where these substances are converted to phenol.

In total we can say that the phenol process has huge potential based on the model. The phenol process is only 18% of the energy costs, the remaining energy costs are the energy gap in the paper process. There is an error in the energy calculations done in Aspen plus modeling, In Aspen Lignin together with some the residue substance and methyl guaiacol had to be put in manually, which means there is an error numbers of these substances. The residue substances is not even a real substance and the error of this substance could be quite large. Even if the error would be large the main energy costs still come from the paper process that needs fuel so the process will still be feasible.

My first recommendation is that a batch experiment should be performed on a larger scale than 5g of lignin, then all the products should be determined, also the gaseous substances. By doing this the energy calculation could be done in greater detail when all substances are specified.

My second recommendation is that the properties of lignin should be further investigated and then be used as input for aspen, so the error in the calculations is minimized.

If these recommendations are done, a new model could be created and then substances like O-cresol, P-cresol and catechol should be purified just like phenol. This would make the process much more attractive from an economical point of view.

References

- [1] <http://www.paperonweb.com/wood.htm>, 11-6-2010
- [2] D.A.I. Goring, The physical chemistry of lignin
- [3] Lignin, *How to breakdown lignin, several techniques*. Power point presentation by A. Kloekhorst, E. Heeres, T. Broekhuis
- [4] Environmental report 2001, Stora Enso Kvarnsveden AB
- [5] http://www.engineeringtoolbox.com/wood-density-d_40.html, 11-6-2010
- [6] R. H. White, Effect of lignin content and extractives on the higher heating value of wood
- [7] E. Kienzle, I. Schrag, R. Butterwick, B. Opitz, 2001, Calculation of gross energy in pet foods: new data on heat combustion and fibre analysis in a selection of foods for dogs and cats.
- [8] <http://www.storaenso.com/about-us/mills/sweden/kvarnsveden-mill/facts/Pages/key-facts-of-kvarnsveden-mill.aspx>, 8-7-2010
- [9] H. Pińkowska, P. Wolak, A. Złocińska, 2012, Hydrothermal decomposition of alkali lignin in sub- and supercritical water. Chemical Engineering Journal, Volume 187, 1 April 2012, Pages 410–414
- [10] <http://www.odfjell.com/TollDistillation/Pages/OurDistillationColumns.aspx> 22-7-2-2012
- [11] <http://www.icis.com/chemicals/phenol/price-reporting-methodology/> 14-05-2012
- [12] <http://statline.cbs.nl/StatWeb/publication/?DM=SLNL&PA=37215&D1=0-2&D2=%28I-11%29-I&VW=T>, 10-7-2012
- [13] http://www.icispricing.com/il_shared/Samples/SubPage81.asp 21-6-2010

Appendix A:

To the left side of the picture of the paper mill the energy use in the different forms and used raw materials, these numbers are used in the calculation in appendix B.

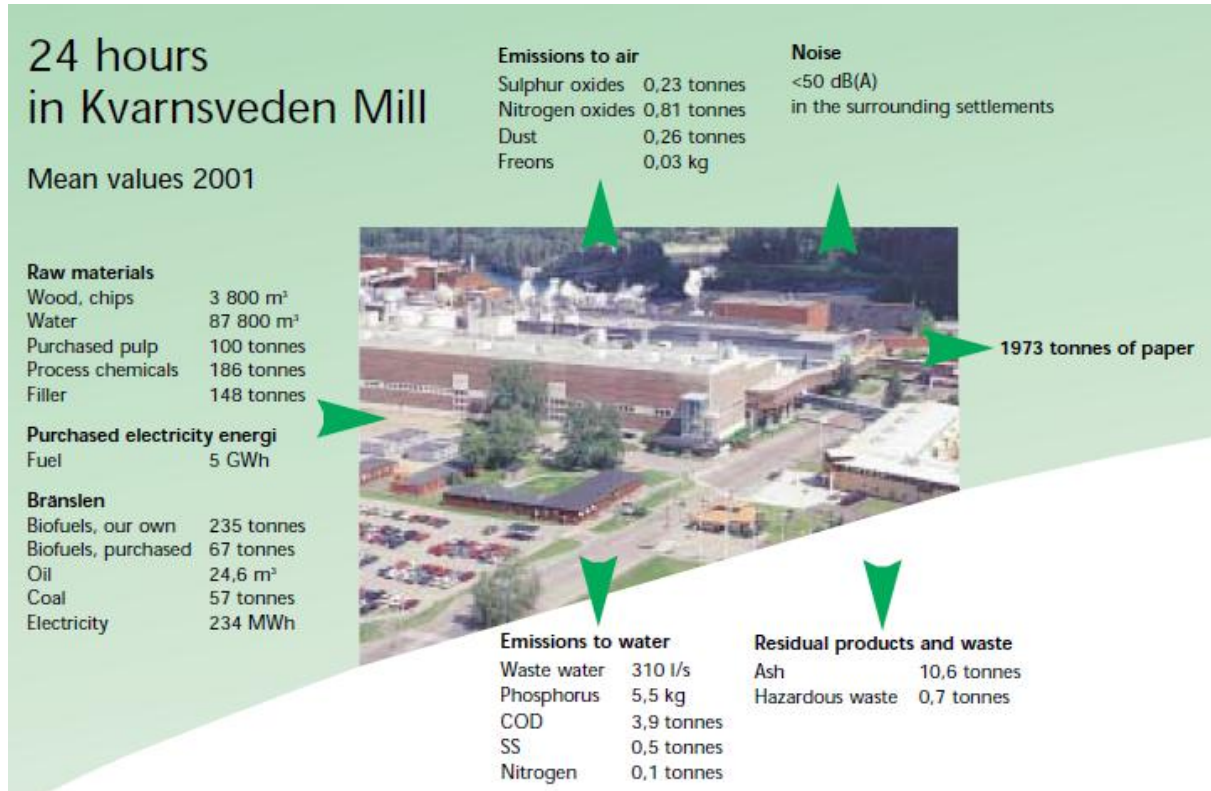


Figure 13. energy use for the paper production in the Kvarnsveden Mill [4]

Appendix B:

The table shows the energy calculation of the information from the kvarnsveden mill from appendix A.

biofuel	302000	kg	20	MJ/kg	6040000	MJ
oil	24.6	m3	34	MJ/l	836400	MJ
coal	57000	kg	31	MJ/kg	1767000	MJ
electricity	234	MWh			842400	MJ
electricity	5000	MWh			18000000	
					27485800	MJ
					27485.8	GJ/day
					1145	GJ/h

table 10. amount of energy produced by the oil, coal and electricity

Appendix C:

In the table the different produced products are shown at different temperatures and a time in the reactor of 0 minutes or 240 minutes. The column to the right at 663K and 240 minutes contains the data used for component input of the project.

Table 1
Composition of the SM fractions obtained from alkali lignin hydrothermolysis.

RT ^a	Compound	T _r (K), t _r (min) Share in the SM fraction (area %)							
		553, 0	553, 240	643, 0	643, 240	653, 0	653, 240	663, 0	663, 240
9.47	Phenol	0.7	2.1	2.0	5.8	3.9	8.2	9.0	11.9
9.74	Guaiaacol	41.9	28.3	27.3	9.5	24.4	8.3	21.1	13.8
10.19	<i>o</i> -Cresol	–	–	–	2.9	1.2	4.0	4.1	6.2
10.70	<i>p</i> -Cresol	–	0.5	1.0	5.5	3.0	4.3	5.3	9.1
10.77	3-Methylguaiaacol	–	–	0.6	0.6	1.1	3.7	2.2	6.2
11.23	4-Methylguaiaacol	2.1	6.2	10.2	3.7	5.7	2.6	4.3	8.0
11.37	Dimethylphenol	–	–	–	1.9	1.0	2.6	2.1	4.2
11.89	Dimethylphenol (isomer)	–	–	–	0.8	0.3	1.3	0.1	0.8
11.95	4-Ethylphenol	–	0.3	0.5	1.9	1.1	3.9	2.5	5.3
12.41	4-Ethyl-2-methoxyphenol	3.2	4.6	6.3	2.3	3.6	1.4	2.0	0.1
12.55	1-Ethyl-4-methoxybenzene	–	–	–	0.7	–	0.5	0.2	1.8
13.05	3-Ethyl-5-methylphenol	–	–	–	–	–	0.7	0.8	1.4
13.15	3-Methoxycatechol	0.1	0.7	0.5	–	–	0.6	1.3	2.0
13.30	3-Methoxyphenol	–	–	0.5	–	–	–	–	–
13.55	2-Methoxy-methyl-ethylphenol	–	0.9	0.8	0.8	–	–	–	–
13.77	Catechol	1.3	10.3	8.5	31.3	15.7	32.8	14.2	12.0
13.89	2,6-Dimethoxyphenol	–	0.8	0.7	–	–	–	–	–
14.26	3-Methylcatechol	–	–	0.7	6.6	6.7	5.1	6.2	3.6
14.76	4-Methylcatechol	–	1.6	1.7	14.4	18.0	11.0	13.4	8.7
15.19	Vanillin	17.9	7.0	10.7	0.8	0.8	–	0.3	–
15.21	4-Ethoxyphenol	–	–	–	0.8	1.8	–	1.3	0.1
15.71	2-Methylresorcine	–	0.7	–	–	–	–	–	–
15.85	4-Methylresorcine	–	0.9	1.0	6.4	7.5	5.0	4.2	2.1
15.91	2-Methoxy-4-propylphenol	2.1	0.7	0.9	–	–	–	–	–
16.08	4,5-Dimethylresorcine	–	–	–	0.6	1.1	–	0.2	–
16.18	1-(4-Hydroxy-3-methoxyphenyl)ethanone	8.8	5.3	5.7	–	0.5	–	0.4	0.1
16.46	4-Hydroxybenzaldehyde	1.1	0.7	0.9	–	–	–	–	–
16.79	1-(4-Hydroxy-3-methoxyphenyl)propanone	10.6	9.6	7.1	–	–	1.9	0.3	1.5
16.85	4-Propylcatechol	–	0.7	0.5	2.6	2.8	2.0	3.8	0.3
16.89	3-Methoxy-4-hydroxybenzyl methyl ether	–	1.2	0.9	–	–	–	0.3	–
17.15	4- <i>tert</i> -Butylbenzene-1,2-diol	0.7	0.7	0.6	–	–	–	0.1	0.6
17.31	4-(3-Hydroxy-1-propenyl)-2-methoxyphenol	1.0	0.5	1.0	–	–	–	–	–
18.19	Vanillic acid 8.7	15.9	9.8	–	–	–	–	–	–

^a Retention time (min).

table 11. the produced product of the experiment of *Piñkowska et al.*[9]

Appendix D:

Here the calculation of the energy use of the process are shown, numbers are based on the results from the Aspen model. table 12 shows that all the energy of heatexchanger H101 is recovered in H102. So only the energy of pump 101 and the energy of the reactor R101 has to be supplied extra.

ID	energy use (kW)
P101	432
H101	17061
R101	2378
H102	-17061
total	2810

table 12. energy in the reaction part of the process

In the purification part an assumption is made that 80% of the energy of the condenser is used again in the reboiler, this is done for distillation columns S103 to s107. S101 is the flash vessel, it is assumed that the energy is lost here, S102 could be used but this is a small number. The largest share of energy in the purification part is in S103, where the MIBK is separated from the organic compounds.

ID	energy use (kW)	Recovered energy (kW)
S101	-5300	0
s102	83	83
s103	-18612	3446.4
	18336	
s104	-1730	416
	1800	
s105	-1332	289.4
	1355	
s106	-1928	389.6
	1932	
s107	-247	57.4
	255	
total		4681.8

table 13. recovered energy in the purification part.

Appendix E:

Table 14 shows the amount of energy that can be provided by burning the components of the process and be compared with the energy by burning the lignin. The heat of combustion numbers for catechol, O-cresol, P-cresol, guaiacol and dimethyl phenol are taken from Aspen Plus modeling. An assumption is made that methyl guaiacol has the same heat of combustion as guaiacol and the residue component is assumed to have the same heat of combustion as lignin. These numbers could be a bit different but all heat of combustion numbers lie between 24000 and 34000 kJ/kg, so it will lie in the right range.

stream s9	massflow (kg/h)	J/mol	g/mol	kJ/kg	GJ/tonne phenol	kW
Catechol	1019.4	2.73E+09	110.1	24823	29.77	7029
Guaiacol	689.2	3.41E+09	124.14	27453	22.26	5256
O-cresol	1.6	3.53E+09	108.14	32624	0.06	14
P-cresol	199.6	3.52E+09	108.13	32572	7.65	1806
Dimethyl phenol	477	4.12E+09	122.11	33740	18.93	4471
methyl guaiacol	2716.9	3.41E+09	138.14	24671	78.86	18619
residue	5666.4			25500	169.99	40137
				total	327.52	77331
stream s11	massflow (kg/h)	J/mol	g/mol	kJ/kg	GJ/tonne phenol	kW
Catechol	0	2.73E+09	110.1	24823	0.00	0
Guaiacol	643.8	3.41E+09	124.14	27453	20.79	4909
O-cresol	173.6	3.53E+09	108.14	32624	6.66	1573
P-cresol	565.6	3.52E+09	108.13	32572	21.67	5117
Dimethyl phenol	1584.4	4.12E+09	122.11	33740	62.89	14849
methyl guaiacol	0	3.41E+09	138.14	24671	0.00	0
residue	0			25500	0.00	0
				total	112.02	26449.50
stream s13	massflow (kg/h)	J/mol	g/mol	kJ/kg	GJ/tonne phenol	kW
Catechol	0	2.73E+09	110.1	24823	0.00	0
Guaiacol	0.2	3.41E+09	124.14	27453	0.01	2
O-cresol	341.8	3.53E+09	108.14	32624	13.12	3098
P-cresol	0.2	3.52E+09	108.13	32572	0.01	2
Dimethyl phenol	4.6	4.12E+09	122.11	33740	0.18	43
methyl guaiacol	0	3.41E+09	138.14	24671	0.00	0
residue	0			25500	0.00	0

				GJ/tonne phenol	kW
total				13	3144
total of streams				453	106925
lignin	20000	total lignin	25500	600	141667
energy gap				147	34742
percentual (%)				75	

Table 14. Energy supply from the restproducts and calculation of the energy gap