# CPD NR 3279

Conceptual Process Design

**Process Systems Engineering**
DelftChemTech – Faculty of Applied Sciences
Delft University of Technology

# Cellulose Production Plant from Wood Chips


| | | **Tel.** |
|---|---|---|
| Peter van Beijeren Bergen en Henegouwen | st1013777 | 071 – 5211267 |
| Bianca Breure | st1013831 | 0186 – 662494 |
| Vincent van Hijkoop | st1013939 | 079 – 3611636 |
| Maaike Kroon | st1013998 | 015 – 2560943 |
| Warbout Tesselaar | st1013940 | 0174 – 294647 |


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## Preface

We would like to thank all the people and companies who made a contribution to our project. Especially the following persons deserve a word of gratitude. First of all Dr. Ir. Hedzer van der Kooi for his guidance during the creative sessions. We would also like to thank Mr. B. Kortekaas for his hospitality at Norske Skog Parenco and the great guided tour over the plant and Mr. H.M.C. van den Boogaard (Van den Boogaard Digital Printing, Uitgeest) for creating this opportunity for us. Furthermore we thank Dr. Ir. L. Petrus, Dr. Ir. H.J.P. Haan and Dr. Ir. M. Noordermeer from Shell Global Solutions for giving us the assignment and their quick response on our questions. During the meetings we learned a lot over process design in practice. For the participation in the kick-off meeting and the BOD meeting we would like to thank Ir. P. Swinkels and Drs. D. Grunwald.

## Summary

In this report a design was made for a plant that produces 100 kton/a cellulose (pulp) out of willow wood chips, by using Alcell technology. The Alcell technology dates from 1978 and the patent has expired. This technology is based on the separation of cellulose from wood by extracting the lignin and hemicellulose with an alcohol-water mixture. The Alcell process has never been commercialized yet due to the high investment costs and the lower quality compared to the existing Kraft pulp. However pilot plants have been attempted. The Alcell technology can only be attractive if valuable by-products are produced.

In our design we tried to make the Alcell process more attractive by the following means: we decided to use a pretreatment step before the extraction to make the wood more accessible to the solvent. Also, we have implemented a solvent and by-products recovery system. We decided to produce biogas as a by-product because of the robustness of the process. The lignin out of the wood and part of the biogas provides the nessecary amount of energy to render the process self-supporting in energy. The plant is on-stream for 8000 hours per year.

The quality of the produced pulp is as close as possible to the quality of Kraft pulp. The market for cellulose in Europe is unsaturated. The shortage of pulp in Europe is about 6,500,000 metric tons per year, and this amount has to be imported. The plant we have designed produces 100,000 metric tons a year and therefore the impact on the market can be neglected.

The design is economically feasible. The total investment costs are 82 million euros. The plant life times is taken as 20 years, 2 years of design and construction included, because of the relatively high investment costs. The sensitivity of the economic criteria to a 10% increase and decrease in Total Investment Cost is relatively low, compared with the sensitivity to fluctuations in the pulp or wood chip prices. This is not surprising because pulp is our major product and wood chips are our only raw material. The Total Investment Cost is very large and therefore a 10% change, has relatively little influence on the economic performance of the plant. At a pulp price of 550 €/ton and a wood chips price of 60 €/ton, the Pay Out Time is 10.3 years with a Discounted Cash Flow Rate of Return of 9.7%. The economic situation might improve, because of the possibility of subsidy for producing biofuels.

The major strengths of our design are the facts that the design is economically feasible and sustainable. Weaknesses include an off spec product (quality of Kraft pulp is not reached), an unproven technology (Alcell) and the use of methanol at high pressures. To improve the situation, a multistage washer can be used to reach the demanded quality, although it might be expensive and less efficient. We recommend a further study to the kinetics of delignification. By means of a HAZOP we think we have provided an insight into necessary safety measures.

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# 1 Introduction

In this CPD-project a conceptual process design is made for a plant that produces cellulose from wood chips. The principals of this project are Dr. Ir. L. Petrus, Dr. Ir. H.J.P. Haan and Dr. Ir. M. Noordermeer from Shell Global Solutions International, OGIR/1. The project is part of Shell's initiative to find processing routes for exploiting renewable feed stocks for energy and chemical feedstock generation. We were guided by Dr. Ir. H.J. van der Kooi, Ir. P.L.J. Swinkels and Drs. D. Grunwald.

The project is based upon an older process to split wood into its main components, namely the Alcell process of which the patent (ref. 80) has just expired. The Alcell organosolv process uses an alcohol-water mixture as 'organosolv' medium to dissolve the lignin and hemi-cellulose from the wood (see appendix 1.1). The remaining cellulose would serve as high quality paper pulp. This process should have been a major competing route to the Kraft process, which is still the dominant process in the industry. However the Alcell process has never been commercialized. The Alcell process has several advantages over the Kraft process, but requires a large investment (ref.5, Young). Finding attractive outlets for hemicellulose and lignin would make the Alcell process even more interesting.

Several constraints have to be considered during the design stage:

- The feedstock consists of wood from willow trees, which are to be grown in the overflow areas next to Dutch riverbanks.
- The plant has to produce 100 kton/a cellulose.
- The quality of the cellulose (pulp) should be as close as possible to that produced in the Kraft process. Important parameters are the lignin content of the cellulose and the chain length.
- The plant should be self-supporting in energy, which has to be supplied by the feedstock or by-products.
- Valuable by-products will make the process economically feasible.
- Any inorganics entering the process with the feed should preferably be recycled to the fields as fertilizer.

The project description is added as appendix 1.5

Sustainability is becoming a more and more important factor in the process industry. Our design contains also a lot of sustainable aspects. The most important aspects arise from the design constraints.

First of all sustainability is inseparably connected to the closing of the natural cycles for components as minerals and carbon. Therefore the recycling of the minerals to the fields is not only useful for us as fertilizer, but also closes the minerals cycle. The sustainable aspect of being self-supporting in energy supply lies in the fact that this means that all the required energy is produced from wood. Since wood is a renewable energy resource the emitted carbon dioxide can be transformed back to biomass by nature. This closes the carbon cycle.
And the third important aspect is that our technology is based on the Alcell process. This implies that during the production process there is no need for environmentally harmful chemicals like sulfur compounds used in the current Kraft processes.

As said before the Alcell technology has never been commercialized, although a lot of research has been performed. The latest versions of the Kraft process use continuous digesters (see appendix 1.2). A continuous digester using Alcell technology doesn't have to be as complicated as a Kraft continuous digester, but it is a new technology. Also the combination of steam explosion (as a pretreatment step) and the organosolv process has never been used before. Nevertheless there do exist processes that solely use steam explosion to produce pulp with a high kappa number.
Wood contains more components than cellulose (see appendix 1.3 and 1.4) and these other components can be converted to byproducts. The design contains a few new features for producing pulp and therefore the investment contains some risk. The byproducts of the plant should therefore be produced using simple and robust technology. In this way the byproducts can compensate some of the risk present in the core of the process. A lot of different byproducts were investigated. The constraint of being self-supporting in energy is an important criterion for the selection of the byproducts. Lignin will be burnt and hemicellulose will be converted to biogas. Lignin doesn't deliver enough energy to run the whole plant and the produced biogas can now partly be used as fuel. The remainder of the produced biogas (about 40 kton/a) can be sold and a subsidy can be awarded because this is a green energy source.

No single organosolv pulping method fulfils all the requirements for a process capable of replacing the Kraft process. Alcohols are solvents with high vapor pressures. This leads to high pressures in digesters, which have to be redesigned. The simplicity of the recovery cycles depends on the number of by-products that are to be recovered. The recovery of by-products is necessary to balance the economy of organosolv processes, but every product typically adds at least one unit operation to the recovery cycle. Some by-products, like alcohols and organic acids, are not especially valuable, but can be easy to produce and separate. Some by-products, for example lignin, are produced in such large amounts that it is difficult to find markets for them.
The optimal size of an organosolv pulping plant seems to be significantly smaller than the optimal size of a Kraft pulping plant. This is mainly due to the fact that no recovery boiler is needed in organosolv processes. It is therefore to be presumed that an organosolv pulping plant will be built in an area with limited forest resources. The most probable recovery method in organosolv processes is distillation, which is a unit operation with a high thermal energy consumption.

The raw materials used for paper production nowadays consist mostly of recycled paper and Kraft pulp. The quality of paper made from recycled paper will always be less than the quality of paper made from wood pulp. We have visited a paper producing plant from Norske Skog in Renkum where newsprint paper is produced. The process Norske Skog uses showed little similarities with our design, because they make newsprint paper for which a lower pulp quality can be used. Nevertheless similarities were present in parts of the process like the furnace, the screw presses and hydrocyclones. Furthermore we got a good impression of the scale of equipment and of the materials (woodchips and pulp) used.

The market for pulp in Europe is far from saturated, as can be seen in figure 1.1.

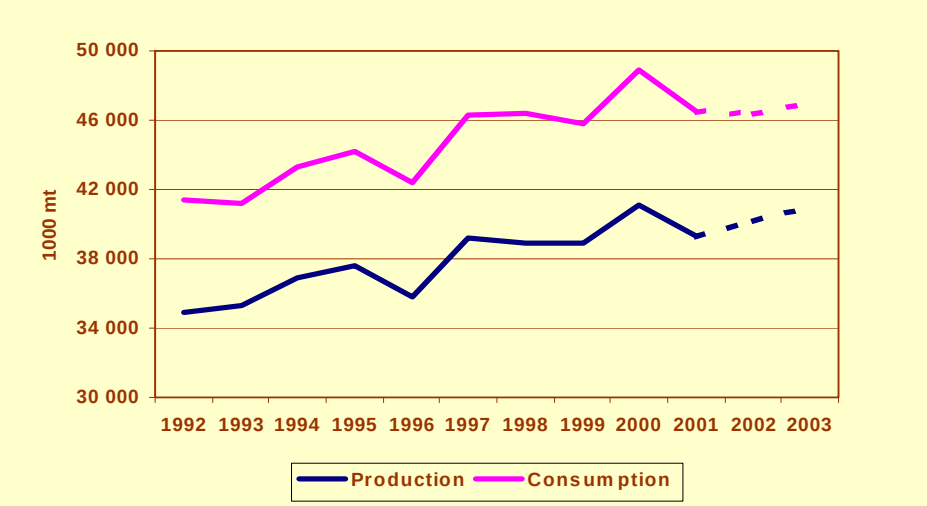

Figure 1.1: European market for wood pulp (Source: ref. 104)

According to dr. P. Ince (ref. 104) the shortage in 2001 in Europe of wood pulp is about 6,500,000 metric tons (see figure 1.1). Because of this shortage a lot of wood pulp is imported. For example from Northern America where the pulp market is exactly opposite to the European market. The plant we have designed produces 100,000 metric tons a year and therefore the impact on the market can be neglected.

The complex structure and composition of wood made it difficult to perform flow sheet simulations. In practice a lot of experimental tests should be performed to find reliable data on for example the kinetics of delignification. Willow wood is not used very often to produce pulp. Therefore we were forced to use data from other wood sorts.
None of us had any experience with pulp or wood processing. Therefore sometimes things were difficult to imagine and visualizations were made, e.g. pulp by dissolving snipes of paper in water. Also we were not familiar with a lot of the equipment used in the pulp & paper industry and therefore an excursion was organized to Norske Skog Parenco in Renkum.
However, the fact that we were not used to the equipment and terms used in this industry gave us an advantage. During the brainstorm sessions we didn't have any reference points and therefore could think freely in all directions.

# 2 Process Options & Selection

The way to solve a design problem is using a hierarchical method, in which first simple solutions are developed for the design problem and then successive layers of detail are added.

## *2.1 Level 1: Plant type and connections*

In this level a decision is made about the mode of operation of the plant (batch versus continuous) and possible connections with other plants.

The main section of the plant for cellulose production from willow wood in the Alcell technology is the extraction section. In this section the extraction can take place continuously as well as batch-wise. We have chosen to operate the extraction continuously (see appendix 2.1).

The rest of the process of pulp making from willow wood chips is also continuous, because the production rate of the plant is high enough to warrant a continuous production (100 kton/a pulp). Moreover during the process no materials are handled that rapidly foul the equipment and the slurries are pumped at sufficient high flow rate to make sure that the solids don't settle out of the suspensions and plug the equipment. There don't seem to be any further operational problems.

The willow trees don't have a constant composition. This is dependent on weather and location. This problem can be solved by mixing, amount of water added in the process, continuous quality control and small changes in cellulose purification and downstream processing.

The plant to produce cellulose from willow wood is a stand-alone plant. It is possible to combine this plant with a papermaking factory, where the cellulose is used to produce paper. In this case the pulp moisture content shouldn't have been reduced, because the first step in producing paper is the adding of water. It is however not an option for the principal and therefore the plant is a stand alone plant.

## *2.2 Level 2: Input/output structure:*

In this level a decision is made about the entering and leaving streams of the process. We focus our attention on what raw materials are fed to the process and what products and byproducts are removed.

The raw materials in our process are willow wood, methanol and water.

- The willow wood is delivered in the form of chips from 3x3x1 cm. The chips cost 60 €/ton (ref. 110)
- Methanol and water are used as solvent (see further on and appendix 2.2). The methanol/water ratio is 75:25 (see appendix 2.3). After the extraction the solvent is recovered. Because methanol is formed during the process, there is a compensation for losses in the recovery of methanol.

The products and byproducts are pulp (mainly cellulose), water and carbon dioxide, biogas, biomass and minerals.

- The quality of the pulp should be as close to the specifications of the Kraft process. This means that the produced pulp must not contain more than 2.7 w% lignin and the molar mass of cellulose should not drop far below $2 \cdot 10^5$ g/mole, which is equal to Kraft quality pulp, see appendix 1.2. The cellulose we produce has a molar mass of about $1.5 \cdot 10^5$ g/mole, which is lower than intended, but still usable (ref. 1, Biermann). This is a characteristic of organosolv pulping processes (ref. 95 and ref. 5). Moreover the hemicelullose content and shive content may not be too high. Therefore before leaving the plant the pulp is screened and subjected to a quality control (see appendix 3.3). The pulp leaving the plant has a 6% moisture content.
- The lignin is used as fuel to generate steam to supply heat and electricity for the process. Therefore the lignin is burnt in a furnace and converted to water and carbon dioxide. Since there isn't a reliable, attractive outlet for lignin and since the process should be self-supporting in energy, this is the best use for lignin. To transport the heat, steam is generated by burning lignin. To make up for steam losses boiler feed water (BFW) has to enter the process.
- The hemicellulose, small amounts of cellulose and the extractives are fermented to biogas (mainly methane and carbon dioxide). In appendix 2.4 other byproducts are evaluated as well, but the biogas production is the most robust and the least capital intensive. An interesting option for expanding the chosen option is given in appendix 2.5.
- The produced biomass in the fermentation is used as cattle feed. This is a standard and reliable outlet for biomass.
- The remaining aqueous wastewater stream with minerals is used as fertilizer for the willow trees. The COD of this stream may not be higher than 100 ppm. This is because the minerals from the willow wood eventually end up mostly in this wastewater stream. To meet the requirement of a closed mineral cycle, this water has to be fed back to the trees, where the minerals can be taken up again.
- Because heat is generated at certain places in the process, cooling has to take place there. For this purpose cooling water (CW) has to enter and leave the process.

The most important decision made here is the choice of byproducts. In this case the choice is made to produce biogas. This has been done, based on the following selection criteria:

*Value of byproducts*: Biogas € 0.23/$m^3$ (ref.79)
Density 0.72 kg/$m^3$
Price € 0.32/kg
The value is low, but all components of hemicellulose can be converted.

*Proven Technology*: All the technology is very well proven.

*Waste*: The waste will be only biomass. All the components of the hemicellulose can be converted to methane.

*Complexity of process*: Simple; because the microorganisms are very stable, methane will be produced as long as the reactor is anaerobe; no extreme conditions are necessary. Furthermore the separations are easy (methane from water and biomass from water).

*Process costs*: The process costs should be low because the separation is easy. Methane is produced as a gas and will leave the reactor at the top. If the hydrolysis of hemicellulose is performed biologically than the process costs will be even lower. All the other alternatives make use of a chemical hydrolysis at 180 °C. The biological hydrolysis can be performed in the biogas reactor at temperatures of 40 °C. The only problem is it takes about two days to perform the hydrolysis with microorganisms (ref.137).

*Health, safety and environment*: Methane is a very explosive gas (Nf = 4, Nr = 0) (ref. 23) and a lot of accidents happen in the normal life. In industry it should be no problem to handle methane. Methane is also toxic (Nh = 1). We should also keep in mind that methane is an important green house gas.

*Purity of byproducts*: The purity of the methane shouldn't be a problem. We expect only $CO_2$ as contaminant. The fossil methane (natural gas) often contains much more pollutants such as $N_2$ and $H_2S$.

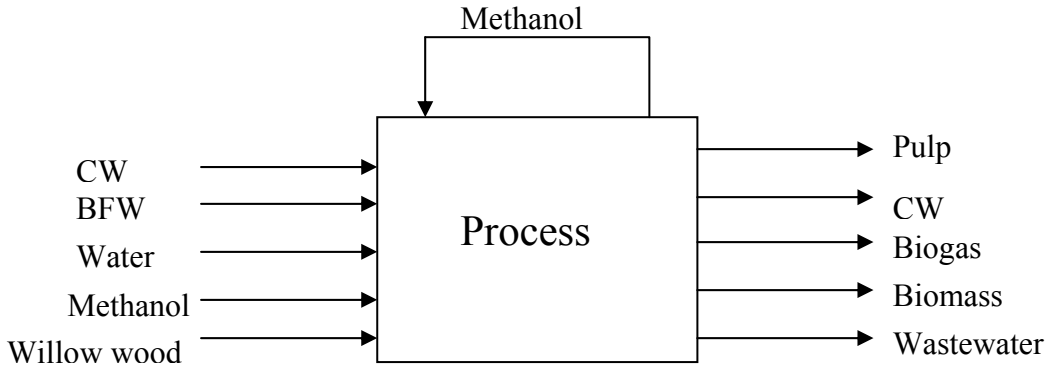


Figure 2.1: Input/output structure of the flowsheet

## *2.3 Level 3: Functional blocks*

The assignment states that Alcell technology has to be used as a starting point. The most important feature of the Alcell process is the extraction with an alcohol-water mixture. Therefore the main block in our process is the extraction stage.
It is possible that the stream of wood chips entering the process is not suitable to enter the extraction stage directly. Therefore a pretreatment section might be necessary. Because of the use of a solvent, there has to be a solvent recovery block. Furthermore the pulp has to have a certain given quality, which means there has to be a pulp purification section. It is stated very clearly in the assignment that the conversion of waste streams to useful byproducts can make the process a lot more viable. Therefore the byproducts formation and recovery section forms an important part of the process.
The process now consists of five functional blocks:

- Pretreatment of the willow wood chips
- Extraction of all components except for cellulose from the wood
- Solvent recovery
- Screening and drying of pulp
- Byproducts formation and recovery

The ordering of these functional blocks is reflected in figure 2.2.

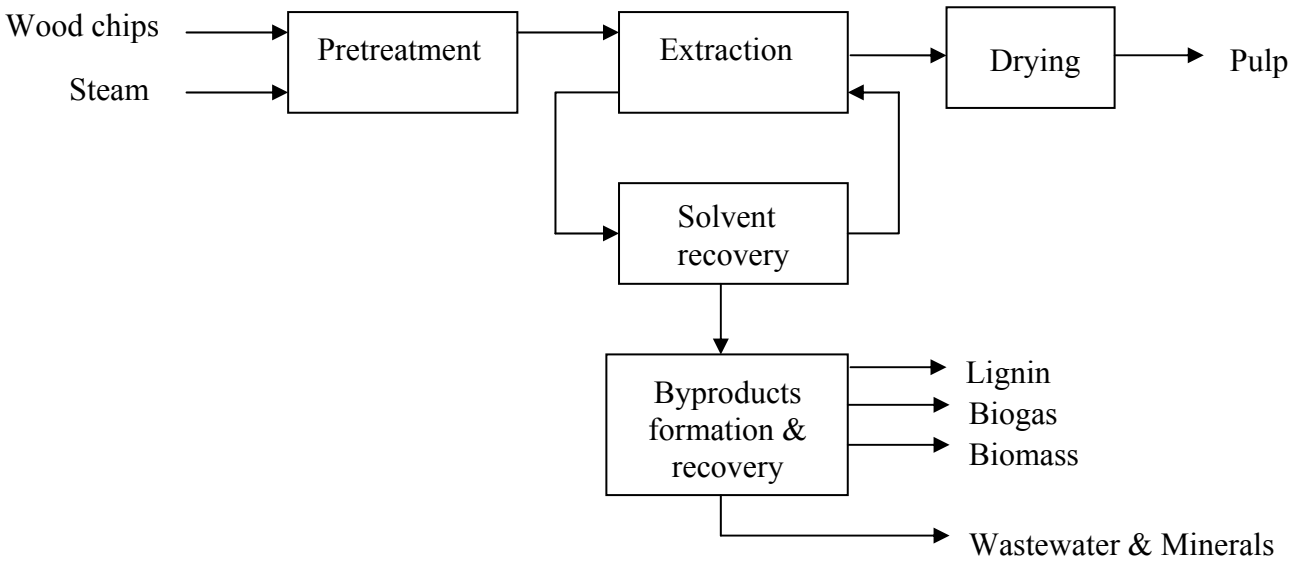


Figure 2.2: Functional blocks of preliminary flowsheet

### 2.3.1 Pretreatment of the willow wood chips

The willow wood enters the process in the form of wood chips. To lighten the severity of the extractor a pretreatment is possible. The use of fungi to pretreat the wood chips to make lignin more accessible during the extraction stage has been evaluated. A possible difficulty would be the duration of this pretreatment, which takes 1 – 4 weeks to complete. This would suggest a large facility. Further information can be found in appendix 5.1.
Another form of pretreatment is steam explosion. In this step the wood chips are treated with steam. By depressurization the steam will explode and the wood cells are torn apart, so the wood is made more accessible for the solvent in the extraction stage. The use of steam explosion leads to lower pulping temperatures and shorter extraction times. More information can be found in appendix 5.1 and 8.2.
A third option is to further reduce the size of the chips. In this way the chips acquire a larger surface area, making them more accessible to the extraction liquor (see appendix 5.1).

### 2.3.2 Extraction of all components except for cellulose from the wood

In the assignment it was given that the process had to be based on the Alcell process (see appendix 1.1), and therefore the process has to have an extraction step. The extraction stage is one of the main parts of the process. Cellulose has to be separated as much as possible, to fulfill the quality requirements. This can be done by dissolving cellulose only, leaving all other components, or by dissolving all other components, leaving cellulose. Solvents for cellulose are given in appendix 2.6.
Because all solvents for cellulose (especially those that can dissolve cellulose at ambient conditions) are either very toxic or very expensive, we have chosen not to investigate this option any further.
Lignin and hemicellulose can be removed by hydrolysis, followed by dissolving and extraction of the lignin and hemicellulose. The rate-determining step here is the delignification rate. The delignification is approximated by a first order exothermic reaction. The delignification can be catalyzed with an earth alkali metal catalyst, for

example calcium chloride. We have chosen not to use a catalyst, because it is very difficult to recover the catalyst (see appendix 2.7).

The extraction is done with a mixture of an alcohol and water. The solvent selection has been based on the following criteria:

- Quality of the pulp (lignin content)
- Costs of solvent
- Safety, health
- Environment
- Ease of recovery (boiling point, azeotrope formation)
- Self-supplying
- Pressure needed
- Corrosive

To enable this decision a number of physical properties and extraction data has been gathered on three candidate solvents: methanol, ethanol and ethylene glycol. The data are summarized in table 2.2. A summary of more possible solvents can be found in appendix 2.2.

Table 2.2: Physical and extraction data for methanol, ethanol and ethylene glycol

| | *Methanol* | *Ethanol* | *Ethylene glycol* |
|---|---|---|---|
| Kappa number | 18 | 27 | 18 |
| Costs | 0.21 €/kg | 0.55 €/kg | 0.53 €/kg |
| MAC-value | 200 ppm<br>260 mg/m$^3$ | 500 ppm<br>1000 mg/m$^3$ | 20 ppm<br>52 mg/m$^3$ |
| Emission standard | | | |
| Nf | 3 | 3 | 1 |
| Nh | 1 | 0 | 0 |
| Nr | 0 | 0 | 0 |
| MF | | | |
| Boiling point | 338 K | 351 K | 471 K |
| Azeotrope | No | Yes (97% ethanol) | No |
| Formation | Yes | Possible | No |
| Pressure needed | 40 bara | 30 bara | |
| Corrosive | No | No | No |

From this table an analysis can be made to select the best solvent, which is given in table 2.3.

Table 2.3: Selection matrix for solvent selection

| | *Methanol* | *Ethanol* | *Ethylene glycol* |
|---|---|---|---|
| Quality | ++ | +/- | ++ |
| Costs | ++ | - | - |
| Safety | - | + | -- |
| Environment | - | + | - |
| Ease of recovery | ++ | + | - |
| Self-supply | ++ | + | -- |
| Pressure | -- | - | +/- |
| Corrosive | + | + | + |

From table 2.3 we draw the conclusion that methanol is the solvent giving the best results, but requiring more attention for safety problems. Because the pulp quality, according to the assignment, has to be as close as possible to that of the Kraft process, we have chosen for methanol as solvent.

### 2.3.3 Solvent recovery

After the extraction, pulp, dissolved solids and solvent have to be separated. The separation of the solvent from the pulp requires the application of a solid-liquid separation step.
After pulp and extract are separated, the solvent has to be separated from both pulp and extract. According to the recovery heuristics (ref Douglas) the most plentiful component is first recovered. This will reduce the size of the equipment in further recovery steps. Moreover the recycle streams must be recovered first to minimize the losses. So, in our case methanol is recovered first. This can be done with a simple adiabatic flash, if necessary followed by a distillation column to remove the excess amount of water.

### 2.3.4 Screening and drying of pulp

The cellulose that will be left after extraction has to be screened and dried and the solvent has to be recovered. This is also the stage where product quality will be measured and controlled (see appendix 3.3). Important parameters are the strength and lignin content of the pulp, because the pulp is used to produce paper.
The screening process checks whether the cellulose pulp has a uniform composition and doesn't contain any lumps of unconverted wood. Normally this process takes place after the extraction stage. In our case we have a quite severe pretreatment (steam explosion) in which some pulping takes place already, and therefore it is possible to screen after this pretreatment, which we will do.

### 2.3.5 Byproducts formation and recovery

The solvent will contain various components after the extraction. Lignin, cellulose, hemicellulose, minerals and extractives (such as terpenes and phenols) are present in this stream. The first thing to do is to recover as much solvent as possible and recycle it back to the extractor. When the methanol is flashed off, the lignin will precipitate, because of lower temperature and removal of mainly methanol, while the hemicellulose remains dissolved in water. This stream containing lignin and water with dissolved hemicellulose is removed from the flash as a slurry and sent to a solid-liquid separator. The lignin is removed here. The aqueous stream with mainly hemicellulose will be sent to a fermentor to produce biogas and biomass (from the hemicellulose and extractives) and an aqueous stream with minerals, which will be sent back to the overflow areas to serve as fertilizer for the willow trees.

# 3 Basis of Design

## *3.1 Description of the design*

The project description stated that the capacity of the plant should be 100 kton/a. The raw material that has to be used is willow wood. These trees can be grown in the overflow areas near the Dutch riverbanks. The technology of the design is based on ALCELL technology (ref. 80). Nowadays pulp is mainly produced by plants that are based on Kraft technology (see appendix 1.2). The quality of the produced cellulose should be as close as possible to the quality of the cellulose produced by the Kraft processes. This means that the amount of lignin in the pulp is about 2.7 w% (see appendix 1.2). Other constraints on the design are:

- any minerals entering the process are returned as fertilizer to the fields
- the plant should be self-supporting in energy

Cellulose is one of the main components present in wood. Willow wood consists of 43.6 w% of water, 0.9 w% of minerals and 55.6 w% of organic material. The organic material consists mainly of cellulose, hemicellulose and lignin. Cellulose is the product and the goal is to separate cellulose from the other components. Lignin can be used as fuel and hemicellulose contains a lot of sugars and can therefore be fermented to valuable byproducts.

In the Alcell technology cellulose is separated from the other components by extraction with an alcohol. The extraction is actually a combination of a hydrolysis reactions and an extraction. The reaction is the rate-determining step and therefore high temperatures (180-220 ºC) are applied. Methanol and ethanol are the alcohols most commonly used in experiments on Alcell technology. These alcohols are very volatile and to keep them liquid at these high temperatures high pressures are necessary. Lignin and hemicellulose dissolve in the alcohol. The next thing to do is separating the alcohol with dissolved hemicellulose and lignin from cellulose. How these separations are performed and what will be done with lignin and hemicellulose is not part of the Alcell technology.

Different possibilities for converting hemicellulose to byproducts (see appendix 2.4 and chapter 2) were investigated. The most important selection criteria in the selection of the conversion route to byproducts were the investment costs and the use of proven technology. The core of the process (the extractor) is based on Alcell technology. This technology was patented 20 years ago, but has never been commercialized, so there is some risk for the investors using this technology. The byproducts should take away some of this risk by using proven technology for the conversion of hemicellulose to valuable byproducts.

## *3.2 Process definition*

### 3.2.1 Process concepts chosen

The wood chips enter the process with the following dimensions 30x30x10 mm.

- *Extraction of cellulose or lignin*
  To produce cellulose from wood, one can dissolve either the cellulose itself or all the other components in wood to obtain the cellulose. Solvents for cellulose are sought for (see appendix 2.6), but these solvents are either not specific for cellulose, change the chain length, are expensive or are environmentally harmful. Therefore it is a better idea to dissolve all the other components from the wood. These components are lignin, hemicellulose, extractives and minerals.

- *Pretreatment of wood chips*
  Steam explosion is used as pretreatment. In the steam explosion process high-pressure steam is added to the wood chips. The steam condenses on the wood chips, diffuses inside the wood chips and finally when the pressure is released the condensed steam will rapidly expand and the wood chips are torn apart. The conditions are about 190 ºC and 12.6 bara. At these conditions hydrolysis of the macromolecules present in wood (cellulose, hemicellulose and lignin) takes place. The hydrolysis of lignin and hemicellulose is a favorable process because the molar weight of these substances decreases and the solubility in the solvent in the subsequent extraction stage is increased. For cellulose the hydrolysis is unfavorable. It is unwanted to dissolve cellulose at the extraction stage and the molar mass of cellulose should remain as high as possible to get a good quality pulp. The hemicellulose contains 21.4 w% acetic acid (see appendix 1.4). A part of this acetic acid is released during the steam explosion. Acetic acid catalyses the reactions in the extractor. So the steam explosion not only delivers smaller wood chips (which are better accessible for the solvent in the extractor) but also hydrolyses lignin and hemicellulose and provides a catalyst (acetic acid). The other options for pretreatment can be found in appendix 5.1.

- *Solvent selection*
  A choice for the solvent for the extraction of lignin and hemicellulose from wood chips has to be made. We have chosen a water-methanol mixture (25 w% water) as solvent (see appendix 2.3). The quality of the pulp will be close to the quality of pulp from the Kraft-process. Moreover methanol is easy to recover, because the boiling temperature is relatively low. Methanol is also formed during the hydrolysis of lignin and therefore there is already a compensation for the losses of methanol in the solvent recovery. The choice of which byproducts are produced also plays a role in the solvent selection. If ethanol were produced by fermenting hemicellulose than the solvent losses could be completely covered and therefore ethanol would be a logical choice. A disadvantage of methanol as solvent is that the heating to 190 °C requires an extraction under high pressure (33 bara). Furthermore methanol is a poisonous chemical and forms inflammable vapors at relatively low temperatures. Therefore a pulping process using methanol has to be carefully designed and operated. In chapter 2 a comparison of different solvents for extraction can be found.

- *Extraction mode: Batch vs. continuous*
  A continuous extraction is selected with a cocurrent contact mode. There is no need to bring the fractionated wood chips and the solvent in contact countercurrently, because the mass transfer rate isn't the rate-determining step. The cocurrent contact mode can be easily realized in a continuous form. When a countercurrent contact mode would have been necessary, because of mass transfer problems, the choice between batch and continuous would have been more difficult (see appendix 2.1)
  Furthermore the large capacity of the process and the handled materials (not very fouling material) are important factors to choose a continuous process.

- *Cellulose purification*
  The excess moisture is evaporated in a dryer. The product should contain less than 6 w% moisture.

- *Recovery of solvent, lignin, extractives, minerals and hemicellulose*
  The effluent of the extractor has a temperature of 190 ºC and 33 bara. After the extraction the high pressure and temperature are not needed any more and because of safety considerations lower pressures and temperatures are wanted. Therefore flashing of the solvent not only recovers the solvent but also brings the chemicals to safer conditions. The pressure drops to 1 bar and the temperature to about 70 ºC. The amount of solvent is reduced by about 50 % and therefore the lignin precipitates, not only due to the lack of solvent but also because of the temperature drop. The hemicellulose, minerals and extractives have a higher solubility and remain in the liquid stream. The remaining methanol in the liquid stream is recovered in a distillation column and the bottom stream of this column contains water and dissolved minerals, extractives and hemicellulose.

- *By-products and energy supply*
  Lignin is easily separated from the solvent by precipitation. Lignin can be used as substitute for phenol formaldehyde resin and as binder. The market for this application is not very large. Lignin however is suitable as a fuel for energy supply.
  Lignin doesn't contain enough energy to supply all the energy required. The hemicellulose is converted anaerobically to biogas by bacteria. Biogas is very suitable for energy generation. Besides that the conversion of hemicellulose to biogas is simple and robust. For the production of other byproducts such as ethanol or lactic acid (see appendix 2.4) the demands on the hemicellulose stream are much higher and this stream would have to be chemically hydrolyzed and complex equipment would have been necessary to separate the formed products from water. The separation of biogas from water is of course easy. The extractives are also converted to biogas. The minerals end up in the wastewater and can be returned to the fields.

### 3.2.2 Block schemes

A simplified block scheme can be found in appendix 3.1.

### 3.2.3 Thermodynamic properties

Many of the thermodynamic properties of willow wood could not be found in literature, therefore a lot of estimations had to be made (chapter 4). The enthalpy of formation was estimated with the method of Benson and validated with the enthalpy of hardwoods in the book of Biermann (ref. 1). The specific heat capacity of willow wood was estimated with Kopps law and the Chueh and Swanson method and validated with the book of Walker (ref. 3). Furthermore the solubility of lignin in methanol had to be estimated. This was done on the basis of a given solubility at one temperature (190 °C) and extrapolation to other temperatures. It was not possible to validate this dependency, but the solubility of lignin at 70 °C was validated on basis of the amount of precipitated lignin (ref. 5). Finally the diffusion coefficient of methanol in willow wood had to be estimated. This was done by calculation of the diffusion coefficient of water into wood. The diffusion constant could not be validated with literature.

The data for water and methanol, as well as the vapor/liquid equilibrium for water/methanol were estimated with the computer program Aspen. Water and methanol show interaction, because both molecules are highly polar and attracted to each other. The presence of polar groups and the interaction between molecules means that an activity coefficient model should be used. According to the DECHEMA Data Series (ref. 24) the following models are good for the estimation of the system water/methanol: Margules, Van Laar, Wilson, NRTL and Uniquac. We have chosen to use the NRTL model, because in the DECHEMA Data series the mean deviation of the values of this model from the experimental observed values is the smallest. In appendix 4.2 the use of the NRTL model in V/L-equilibria is validated with the data in the literature.

In the process two reactions take place, namely the hydrolysis of lignin, cellulose and hemicellulose and the bioconversion of monosaccharides to biogas and biomass. It was difficult to find information about the kinetics of the hydrolysis reaction. The hydrolysis of lignin is assumed to be a first order reaction, of which the first order reaction constant is three times higher than the reaction constant of delignification in the Kraft process. This is because we carry out a steam explosion, which cancels diffusion limitation and produces acetic acid, which acts as a catalyst. This is validated by articles by G. Garotte (ref. 35) and San Martin (ref. 68). The bioconversion of monosaccharides to biomass and biogas follows the Monod kinetics for the specific growth rate of biomass (ref. 59).

An extensive overview of the used thermodynamic properties, their estimations and validations can be found in Chapter 4 and the appendices 4.1, 4.2 and 4.3.

### 3.2.4 Pure component properties

A list of pure component properties is given in appendix 3.2.

## *3.3 Basic assumptions*

### 3.3.1 Plant capacity

The cellulose production plant should produce 100 kton (dry) cellulose pulp per year. Since the plant is assumed to be on stream for 8000 hours per year, this means a production of 3.47 kg/s. The pulp quality should be as close as possible to that of the competing Kraft process. The aim was set at 2.7 w% lignin. The pulp eventually contains 5.4 w% lignin. The pulp further contains 85.6 w% cellulose, 3.7 w% hemicellulose and 3.2 w% water. The rest consists of small amounts of organics. All streams crossing the battery limit are defined in tables 3.1 and 3.2. Table 3.1 shows the entering streams and table 3.2 the leaving streams.

Table 3.1: Entering streams crossing the battery limit.

| *Stream name* | *Stream nr.* | *Magnitude [ton/a]* | *Yield [t/t pulp]* |
|---|---|---|---|
| Wood chips | <1> | 420,000 | 3.64 |
| Make-up methanol | <17> | 3,400 | 0.03 |
| Make-up water | <40> | 2,074 | 0.02 |
| BFW | - | 51,350 | 0.44 |
| CW | - | 16,742,880 | 145.08 |

Table 3.2: Leaving streams crossing the battery limit

| *Stream Name* | *Stream nr.* | *Magnitude [ton/a]* | *Yield [t/t pulp]* |
|---|---|---|---|
| Pulp (product) | <32> | 116,210 | 1.00 |
| Biogas (byproduct) | <27> | 25,060 | 0.22 |
| Biomass | <29> | 23,330 | 0.20 |
| Wastewater | <38> | 213,700 | 1.84 |
| Shives | <12> | 2,390 | 0.02 |
| CW | - | 16,742,880 | 145.08 |

### 3.3.2 Location

To determine a suitable location for the plant, a few things should be kept in mind. First of all, it is desirable to construct the plant nearby resources. In this case a spot nearby the Dutch riverbanks would be desirable, because the willow wood is to be harvested in the overflow areas. A second consideration would be the transportation of the final product. If there were a need to deliver relatively dry pulp, this would result in large energy costs, because process water would have to be evaporated. It might be possible to find a location nearby a bleaching facility or a paper mill, which uses an input stream consisting of almost 99% water and 1% pulp. This option would contribute enormously to energy savings in our process. The last reason why it would be profitable to establish a plant nearby the overflow areas is because a side stream of the process, a stream that consists of water with dissolved minerals, could be flown over the land. In this way energy could be saved because there is no need to concentrate the stream first. The minerals could serve as a fertilizer to the trees.
According to Paul Geerts (ref. 106) the yield of (wet) willow wood chips is 100 ton per hectare per year. Because the plant uses 420 kton/a wood chips, the necessary overflow area is 42.0 $km^2$. This is a relatively large area.
Possible locations that fulfill the above mentioned requirements are the areas around Wageningen or Nijmegen. Both cities lie adjacent to a river and nearby overflow areas and paper industry.

### 3.3.3 Battery Limit

The battery limit can be determined using the block scheme in appendix 3.1. Here it can be seen that the wood enters the process in the form of chips. Therefore the cultivation, harvesting and chipping of the willow wood is not taken within the battery limit. Because the willow cannot be harvested all year round and the plant has to operate continuously a wood storage facility is included within the battery limit. The principal stated that the pulp produced should be dry enough for transport, i.e. a moisture content of 6 w%. For this reason a drying operation is included within the battery limit and the pulp crossing the battery limit will have a moisture content of 6% or less. To ensure continuous operation a storage for make-up water (process water) and methanol is also taken within the battery limit. Methanol and process water are not produced within the plant, so these streams do cross the battery limit. Boiler feed water is also process water and can therefore be stored in the same tank as the make-up water. Cooling water is pumped up from the nearby rivers and therefore crosses the battery limit. The produced lignin is burned and therefore doesn't cross the battery limit. The same holds for part of the biogas produced, because this is burned too. The rest of the biogas does cross the battery limit and is sold to a nearby power plant or other plant. In case it is not possible to sell the biogas, it won't leave the plant but will be burned with the rest of the biogas to produce electricity, which can be sold or used for own consumption. The biomass produced will be sold as cattle feed and will therefore cross the battery limit. The wastewater from the fermentor can be used as fertilizer for the willow trees, but since the trees are not grown within the plant, the wastewater stream crosses the battery limit.

### 3.3.4 Definition In- and Outgoing streams

### 3.3.5 Feedstocks

Values are valid at battery limit.

*Wood Chips <1>*
The wood chips are coming from a nearby wood plant in the river overflow area. Because harvesting cannot be done all year round and because continuous operation has to be ensured, a wood storage facility is used.

Table 3.3: Wood chips stream definition

| Stream Name : | | **Wood Chips** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Cellulose | w% | | 27.0 | (1) | (1) See appendix 1 |
| Hemicellulose | w% | | 14.3 | (1) | |
| Lignin | w% | | 12.6 | (1) | |
| Extractives | w% | | 1.7 | (1) | |
| Minerals | w% | | 0.9 | (1) | |
| Water | w% | | 43.5 | (1) | |
| | | | | | (2) Average outside temperature |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 10 | (2) | |
| Press. | Bara | | 1 | | (3) See chapter 11 |
| Phase | V/L/S | | S | | |
| Price | EUR/ton | | 60 | (3) | |

*Make-up Methanol <17>*

Methanol can be bought in various qualities. The main other component in methanol is water. Because in our process water has to be added anyway to make solvent of the right composition, the methanol doesn't have to be very pure. For easy calculations, the methanol stream is taken 100% pure. In reality this percentage will be lower and therefore the make-up water stream <40> will be smaller.

Table 3.4: Make-up methanol stream definition

| Stream Name : | | **Make-up Methanol** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Methanol | w% | 0-100 | 100.0 | (1) | (1) Will be lower in reality |
| | | | | | (2) Average outside temperature |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 10 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | L | | (3) Price is for purity of 99.9% |
| Price | EUR/ton | | 208 | (3) | |

*Make-up Water <40>*

The water used for this purpose is so-called process water. In reality this water is not 100% pure water (demi-water), but since the process already contains far larger

amounts of water from the willow wood, these small amounts in the make-up are not taken into account.

Table 3.5: Make-up water stream definition

| Stream Name : | | **Make-up Water** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Water | w% | 0-100 | 100.0 | (1) | (1) Small amounts of pollution will be present |
| | | | | | (2) Average outside temperature |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 10 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | L | | (3) Standard price for |
| Price | EUR/ton | | 0.5 | (3) | Process Water |

### 3.3.6 Products

*Pulp*

The main product is cellulose pulp. The aim for the specifications was given by the principal. The eventual specifications are given below.

The quality of the pulp leaving the process should be controlled. Therefore samples will be taken from the pulp and a number of quality measuring methods will be used to determine the quality:

- Cellulose molecular weight determination: The cellulose shouldn't have an average molar weight lower than $1.0 \cdot 10^5$ g/mol, because than the strength of cellulose becomes critical. In our process the molar weight of cellulose is about $1.5 \cdot 10^5$ g/mol. The molar weight of cellulose is measured by means of dissolving the cellulose in cupriethylene-diamine.
- Lignin content determination: The lignin content of the pulp may not be higher than 2.7 % (see appendix 3), because than the pulp quality is worse than the quality of pulp from the Kraft process. When the pulp contains more lignin, the pulp is too dark and intensive bleaching is necessary. The lignin content is measured using the Kappa number.
- Moisture content determination: According to Biermann and Walker (ref. 1 and ref.2) the moisture content of pulp shouldn't be higher than 6 w%.

The methods used for the quality control can be found in appendix 3.3

Table 3.6: Pulp stream definition

| Stream Name : | | **Pulp** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Cellulose | w% | | 85.6 | | (1) Higher than actually planned for |
| Hemicellulose | w% | | 3.7 | | |
| Lignin | w% | | 5.5 | (1) | |
| Extractives | w% | | 0.5 | | |
| Minerals | w% | | 0.2 | | |
| Water | w% | | 3.3 | | |
| Methanol | w% | | 0.9 | | (2) Outlet temperature of pulp dryer |
| Acetic Acid | w% | | 0.3 | | |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 84.8 | (2) | |
| Press. | Bara | | 1 | | (3) See chapter 11 |
| Phase | V/L/S | | S | | |
| Price | EUR/ton | | 550 | (3) | |

*Biogas*

The most important byproduct formed is biogas. The biogas is partly burnt to produce energy for the process. The rest crosses the battery limit and can be sold. Because methane is the only valuable component in biogas, the value is calculated with the price for methane only.

Table 3.7: Biogas stream summary

| Stream Name : | | **Biogas** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Methane | w% | 26.3 | 26.3 | (1) | (1) Dictated by stoichiometry of fermentation |
| Carbon Dioxide | w% | 73.7 | 73.7 | (1) | |
| | | | | | (2) Temperature in fermentor |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 40.2 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | V | | (3) Price is that of methane ONLY |
| Price | EUR/ton | | 320 | (3) | |

*Biomass*

When performing a fermentation process biomass is inevitably formed. To make use of this stream it can be sold as cattle feed. Because we are not sure if biomass with this composition can be sold as it is, it is not taken into account in the economical

analysis (chapter 11) and the price is therefore set to zero. This simplification doesn't have a large impact since this is a relatively small stream and probably won't yield a large profit when sold.

Table 3.8: Biomass stream summary

| Stream Name : | | **Biomass** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | | Additional Information |
| | | Available | Design | Notes | (also ref. note numbers) |
| Biomass | w% | | 49.9 | (1) | (1) Assumption of 50% |
| Water | w% | | 49.9 | (1) | water was made |
| Minerals | w% | | 0.2 | | |
| | | | | | (2) Temperature in fermentor |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 40.2 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | S | | (3) Possible markets |
| Price | EUR/ton | | 0 | (3) | have to be found |

### 3.3.7 Wastes

*Wastewater*

Water coming from the fermentor still contains a small amount of minerals and ppm amounts of sugars. The minerals in the water can serve as fertilizer for the willow trees. If the trees are grown nearby this stream doesn't have to be concentrated and can be used as such. The sugar content should not exceed a chemical oxygen demand of 100 ppm to make sure it can be used on the land. Because this stream doesn't have a large economic potential and because it is used as fertilizer for the willow trees that will later enter the process, the price is set to zero.

Table 3.9: Wastewater stream summary

| Stream Name : | | **Wastewater** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Water | w% | 0-100 | 99.5 | | (1) To be used as fertilizer |
| Minerals | w% | | 0.5 | (1) | |
| Sugars | ppm | | <100 | (2) | |
| | | | | | (2) COD |
| | | | | | (3) Temperature in fermentor |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 40.2 | (3) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | L | | (4) Not taken into account |
| Price | EUR/ton | | 0 | (4) | |

*Shives Purge*

A part of the rejects from the screener is purged to avoid accumulation of large unpulped parts in the system. This stream can be sold or burnt. For an economical analysis the fuel value is taken.

Table 3.10: Shives purge stream definition

| Stream Name : | | **Shives Purge** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Cellulose | w% | | 28.0 | (1) | (1) Estimation |
| Hemicellulose | w% | | 16.0 | (1) | |
| Lignin | w% | | 30.0 | (1) | |
| Extractives | w% | | 1.0 | (1) | |
| Minerals | w% | | 0.5 | (1) | |
| Water | w% | | 24.5 | (1) | |
| | | | | | (2) Outlet temperature of screener |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | oC | | 100 | (2) | |
| Press. | Bara | | 1 | | (3) Fuel value |
| Phase | V/L/S | | S+L | | |
| Price | EUR/ton | | | (3) | |

## 3.3.8 Utilities

*Boiler Feed Water (BFW)*

Because the steam cycle in our process isn't closed (water leaves the process in the outgoing streams) a make-up stream to the furnace is needed. This so-called boiler feed water (BFW) is also process water.

Table 3.11: Boiler feed water stream definition

| Stream Name : | | **Boiler Feed Water** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Water | w% | 0-100 | 100.0 | (1) | (1) Small amounts of pollution will be present |
| | | | | | (2) Average outside temperature |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 10 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | L | | (3) Standard price for |
| Price | EUR/ton | | 0.5 | (3) | Process Water |

*Cooling Water (CW) In*

The cooling water used is taken from the nearby river. For this water the standard costs for cooling water are taken. Of course this water will not be 100% pure, but since it runs through a closed system that doesn't interact with the process streams, the pollutions are not taken into account.

Table 3.12: Cooling water (CW) in stream summary

| Stream Name : | | **Cooling Water In** | | | |
|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) |
| | | Available | Design | | |
| Water | w% | 0-100 | 100.0 | (1) | (1) Small amounts of pollution will be present |
| | | | | | (2) Average outside temperature |
| Total | | | 100.0 | | |
| Process Conditions and Price | | | | | |
| Temp. | ºC | | 10 | (2) | |
| Press. | Bara | | 1 | | |
| Phase | V/L/S | | L | | (3) Standard price for |
| Price | EUR/ton | | 0.03 | (3) | cooling water (CW) |

*Cooling Water (CW) Out*

The cooling water mentioned in the previous paragraph has to leave the process again too. Because no chemical interaction takes place between the cooling water and the process streams, this water is not polluted (further) and can therefore be sent back to the river. The only requirement left is that the temperature is not too high. Therefore the stream is first cooled down in a cooling tower. In a cooling tower usually no more than 1% of the water evaporates. Therefore it is assumed that all the cooling water entering the plant leaves the plant again via the river. Because the costs for the cooling water are already calculated with the cooling water in stream, the price of the outgoing cooling water stream is set to zero.

Table 3.13: Cooling water (CW) out stream summary

| Stream Name : | | **Cooling Water Out** | | | | |
|---|---|---|---|---|---|---|
| Comp. | Units | Specification | | Notes | Additional Information (also ref. note numbers) | |
| | | Available | Design | | | |
| Water | w% | 0-100 | 100.0 | (1) | (1) | Small amounts of pollution will be present |
| | | | | | (2) | Maximum temp. allowed in summer |
| Total | | | 100.0 | | | |
| Process Conditions and Price | | | | | | |
| Temp. | oC | | 27 | (2) | | |
| Press. | Bara | | 1 | | | |
| Phase | V/L/S | | L | | (3) | Taken zero, costs taken with inflow |
| Price | EUR/ton | | 0 | (3) | | |

## *3.4 Economic margin*

The margin can be calculated by subtracting the total value of feedstock and process chemicals into the plant from the total value of the products and wastes out of the plant.

A survey of the streams into and out of the plant and their value is reflected in the following two tables.

Table 3.14: Calculation of the Gross Income

| *Compound* | *Mass flow [ton/a]* | *Price [€/ton]* | *Cost [€/a]* |
|---|---|---|---|
| Pulp | 116,200 | 550.00 | 63,910,000 |
| Biogas | 6,566 | 320.00 | 2,101,000 |
| Rejects | 2,390 | 60.00 | 143,400 |
| Biomass | 11,640 | 35.00 | 407,400 |
| Fertilizer (wastewater) | 990 | 150.00 | 148,500 |
| Gross Income | | | 66,710,300 |

Table 3.15: Total Raw Material Cost

| *Compound* | *Mass flow [kton/a]* | *Price [€/ton]* | *Cost [€/a]* |
|---|---|---|---|
| Wood Chips | 420,000 | 60.00 | 25,200,000 |
| Make-up methanol | 3,398 | 208.00 | 707,000 |
| Make-up water | 2,074 | 0.50 | 1,000 |
| Total Raw Material Cost | | | 25,908,000 |

Margin = Total earnings – total cost = 40.8 million €/yr

In this margin the utilities are not included.

Subsequently, the maximum allowed investment at a Discounted Cash Flow Rate of Return (DCFRR) of 10% (r = 0.10) is calculated.

In the first two years only investments are done for construction of the plant, so the cash flow is negative. In the third year the production of pulp starts and the cash flow will be positive. We assumed a plant lifetime of ten years.
The cash flow is equal to the Net Future Value, which can be found in table 3.16. We assumed that the net cash flow for every year from the third year on is constant and equal to 40,800,000 €/yr.

The money earned in any year can be put to work (reinvested) as soon as it is available and start to earn a return. So money earned in the early years of the project is more valuable than earned in later years. Therefore the Net Future Value is corrected to Net Present Value. The results are summarized in the following table.

Table 3.16: Summary of the results

| *Year(n)* | *NFV [million euro/a]* | *Cum. NFV [million euro]* | *1/(1+r)^n* | *NPV [million euro/a]* |
|---|---|---|---|---|
| 0 | 0 | 0 | 1.0 | 0 |
| 1 | -104 | -104 | 0.91 | -94.2 |
| 2 | -104 | -208 | 0.83 | -85.7 |
| 3 | 40.8 | -167 | 0.75 | 30.7 |
| 4 | 40.8 | -126 | 0.68 | 27.9 |
| 5 | 40.8 | -85.6 | 0.62 | 25.3 |
| 6 | 40.8 | -44.8 | 0.56 | 23.0 |
| 7 | 40.8 | -4.00 | 0.51 | 20.9 |
| 8 | 40.8 | 36.8 | 0.47 | 19.0 |
| 9 | 40.8 | 77.6 | 0.42 | 17.3 |
| 10 | 40.8 | 119 | 0.39 | 15.7 |
| Total | 119 | | | 0 |

So the maximum allowed investment at an interest of 10% is 208 million euro. At higher investments the plant isn't economically feasible. In reality, the lifetime of capital-intensive plants is larger than 10 years, so even higher investments can be made.

The total investment turned out to be 82 million euro (see chapter 11). In the calculated maximum investment cost all operating cost were neglected and therefore the maximum investment costs are relatively high compared to the real investment cost.

# 4 Thermodynamic Properties and Reaction Kinetics

## *4.1 Operating window*

In the calculations in this CPD project a lot of values for thermodynamic properties and reaction kinetics were necessary. Some of these values could be found in literature, other values had to be estimated. In this chapter the used data are summarized and critically regarded.

First of all, it is important to realize what the situations are that need to be modeled, and which thermodynamic properties are important in each unit operation. The data used should be valid within the range of the operating conditions. For the various unit operations the operating window is therefore first determined.

Table 4.1: Operating window

| *Unit operation* | *Steam explosion* | *Screening* | *Extraction* |
|---|---|---|---|
| Process conditions | 12.6 bar<br>190 °C | 1 bar<br>100 °C | 33 bar<br>190 °C |
| Equilibrium | V/L/S | L/S | L/S |
| Components | Steam, wood chips, water | Small chips, chives | Chips, water, methanol |
| Residence time | 7 minutes | | 0.64 hours |
| Important (thermodynamic) properties | Saturated steam pressure, heat of evaporation, specific heats, explosion severity, diffusion coefficients | Shive content, shive dimensions | Lignin solubility, kinetics of delignification |

| *Unit operation* | *Lignin separation (hydrocyclone)* | *Solvent recovery (distillation)* | *Fermentation* |
|---|---|---|---|
| Process conditions | 1.4 bar<br>72.9 °C | 1 bar<br>72.8 °C | 1 bar<br>40.2 °C |
| Equilibrium | L/S | V/L | V/L/S |
| Components | Precipitated lignin, water, methanol | Water, methanol | Water, biomass, biogas |
| Residence time | | | 0.96 days |
| Important (thermodynamic) properties | (Difference in) Density, particle size, viscosity | V/L equilibrium water/methanol | Kinetics, reaction enthalpy |

## *4.2 Thermodynamic properties*

As many of the thermodynamic properties could not be found in literature, a lot of estimations had to be made. The wood chips aren't simulated in the simulation program Aspen, but the solvent recovery system is. Therefore especially data about the wood chips had to be estimated, whereas for water and methanol the data in Aspen could be used and validated with data from literature.
In appendix 4.1 the following thermodynamic properties are estimated and validated:

### 4.2.1 Enthalpy of formation of willow wood

The enthalpy of formation for the main components in willow wood can be estimated using the group contribution method of Benson (ref. 20). This is valid for the gas

phase, but we have assumed that these values are also valid for the solid phase, as the enthalpy of sublimation for very large molecules can be neglected, because in the Benson method the error (18-62 kJ/kg) (ref. 20) is significantly larger than the influence of the enthalpy of sublimation (3.15 kJ/kg) (see appendix 4.1). The enthalpy of formation is valid for 25 °C and 1 bar. With the (estimated) specific heat capacity of willow wood the enthalpy of formation is corrected to the actual temperatures in the operating window.
In the literature a value for the enthalpy of formation of willow wood could not be found, though the enthalpy of formation for dry hardwoods (Biermann, ref. 1) only deviates 4% from the estimated value for the enthalpy of formation for dry willow wood. From this we conclude that the estimation is in the right order of magnitude.
If we would use a wrong value for the enthalpy of formation in calculating the enthalpy of all streams, then the error would only have effect on the estimated enthalpies of the produced pulp and precipitated lignin, which have the same uncertainty.

### 4.2.2 Specific heat capacities of water, methanol and willow wood

The specific heat capacities of water and methanol can be found in literature (ref. 21). Because the solvent recovery system is simulated in Aspen, the specific heat capacities of water and methanol as a function of temperature (within operating window) in Aspen are compared to the literature values (see appendix 4.1). The Aspen values differ slightly from the literature. The Aspen values are wrong for lower temperatures (< 40°C), but we didn't use temperatures lower than 70 °C. Therefore we don't think this is a problem in the design. The influence of pressure is not taken into account, because the pressure doesn't have a strong influence on the specific heat capacity.
The specific heat capacity of the organics in willow wood is estimated with Kopp's rule and with the Chueh and Swanson method (see appendix 4.1). These methods gave somewhat different results. The methods can have a deviation of about 10% from the real value (ref. 20), but the accuracy is increased using the average value. The drawback of both methods is that the specific heat can only be estimated for a temperature of 20 °C and not for other temperatures. We will assume that the specific heat capacity of the organics is constant over the operating window, because there is no better information available.
The specific heat capacity of the organics in willow wood was validated by calculating the overall specific heat of the willow wood. This value was exactly the same as in literature (Walker, ref. 3), so our estimation of the specific heat capacity of the organics in willow wood is good.

### 4.2.3 Heat of evaporation of water and methanol

In the steam explosion the heat of evaporation of water at 115 °C and 190 °C is used and in the solvent recovery system the heats of evaporation of water and methanol are used to calculate the amount of heat needed in the evaporator and the amount of energy withdrawn in the condenser.
For the steam explosion the heat of evaporation of water from the literature is used (ref. 18 and 125) and in the solvent recovery system the heats of evaporation from Aspen are used. In appendix 4.1 the Aspen values are compared to the literature

values. In this appendix one can see that the Aspen values correspond to the literature values.

#### 4.2.4 Solubility of lignin in methanol

The solubility of lignin is only found in literature at 195 °C for two molar weights (ref. 5). However the solubility of lignin at lower temperatures is needed to calculate how much lignin will precipitate in the lignin recovery flash. Therefore the solubility at other temperatures will be estimated with the help of an estimation for the enthalpy of fusion and the temperature of fusion. The temperature of fusion is estimated with Fedors' method, because this is the most suitable method for estimating the temperature of fusion for large molecules (ref. 19).
The determined equation of the solubility of lignin in methanol as a function of temperature cannot be validated with literature. However we think our estimate is reasonable, because Young (ref. 5) states almost the same temperature to cool to, to precipitate more than 99.5% of the lignin.

#### 4.2.5 Diffusion coefficients of water and methanol in willow wood

To calculate the maximum size of the wood chips (no diffusion limitations), the diffusion coefficients of water and methanol in willow wood as a function of temperature have to be estimated. In the literature (ref. 97) only an equation for the diffusion of water into wood can be found (see appendix 4.1). We assume water and methanol have the same diffusion coefficient, because the molecules are both small and polar. The diffusion coefficient for methanol in wood cannot be validated with literature.

The viscosity, density, vapor pressures and heat capacity of mixtures were also necessary to calculate the size of the equipment. In appendix 4.1 the methods for calculating these properties for mixtures with known values for pure components are given.

### *4.3 Vapor-liquid equilibria*

In the flashes, dryers and the distillation column the methanol and water (with wood organics) are separated from each other by means of difference in boiling point. Although the water contains dissolved lignin, we assume that this doesn't have a strong influence on the equilibrium, because the molar fraction of lignin is very small compared to the amount of water and methanol.

Water and methanol show interaction, because both molecules are highly polar and attracted to each other. The presence of polar groups and the interaction between molecules means that an activity coefficient model should be used. According to the DECHEMA Data Series (ref. 24) the following models are good for the estimation of the system water/methanol: Margules, Van Laar, Wilson, NRTL and Uniquac. We have chosen to use the NRTL model, because in the DECHEMA Data series the mean deviation of the values of this model from the experimental observed values is the smallest. In appendix 4.2 the use of the NRTL model in V/L-equilibria is validated with the data in the literature. In this appendix one can see that the V/L-equilibrium at 1 bar in Aspen agrees with the V/L-equilibrium in the literature (ref. 24).

## *4.4 Reaction kinetics*

In the process the following reactions take place:

- hydrolysis of lignin, cellulose and hemicellulose
- bioconversion of monosaccharides to biogas and biomass

### 4.4.1 Hydrolysis of lignin, cellulose and hemicellulose

To dissolve the lignin, it has to be hydrolyzed to smaller parts. The hydrolysis of lignin is the reaction of one molecule lignin with one molecule of water to two smaller molecules of lignin:

$$\text{Lignin (s)} + H_2O\text{ (l)} \rightarrow \text{Lignin (s)} + \text{Lignin (s)} \rightarrow \text{Lignin (aq)} \qquad (4.1)$$

However when lignin is hydrolyzed, also part of the cellulose and hemicellulose are hydrolyzed. This is not preferred, because the cellulose molar weight has to be high to warrant a good quality.

First of all it has to be determined whether the hydrolysis reaction is diffusion limited or not. Therefore the diffusion of water and methanol into wood has to be modeled (see appendix 4.3). It seems that without the steam explosion the wood chips are too large, and diffusion limitation would exist. However when steam explosion is carried out before extraction, the wood chips are smaller and diffusion limitation is no longer present.

In the extraction process the rate determining step is the delignification rate and not the dissolving of lignin fragments in the solvent. The delignification is not a single reaction, but a multitude of various bond-breakings of lignin. There is no single kinetic equation for all these reactions. Therefore first order kinetics for delignification are assumed in various handbooks about pulp and papermaking. First order kinetics are also assumed for cellulose and lignin hydrolysis.

The first order reaction constant depends on the temperature in the following way:

$$k = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \qquad (4.2)$$

with:
$k_o$ = reaction constant at infinite temperature($s^{-1}$)
$E_a$ = activation energy (J/mol)
R = universal gas constant (J/(mol·K))
T = absolute temperature (K)

The parameters in the reaction constant for hydrolysis of lignin, cellulose and hemicellulose are only found in the literature for the Kraft process. In the articles by G. Garotte (ref.65) and San Martin (ref. 68) it was found that the reaction constant is 3 times higher when a steam explosion is done before the extraction, because then acetic acid is already present (from the hydrolysis of hemicellulose), which catalyzes

the delignification. With this information the following Arrhenius parameters are estimated (see appendix 4.3):

Table 4.2: Arrhenius parameters for the different components

| *Component* | *$E_a$ (kJ/mol)* | *$k_0$ ($s^{-1}$)* |
|---|---|---|
| Lignin | 128 | $3.5 \cdot 10^{11}$ |
| Cellulose | 108 | $9.0 \cdot 10^{7}$ |
| Hemicellulose | 108 | $9.0 \cdot 10^{5}$ |

We will assume that the hydrolysis reaction can proceed completely. The equilibrium lies completely on the right hand side. This is reasonable, because the amount of methanol and water (molar basis) is more than a million times larger than the amount of lignin in the steam explosion and in the extraction. Therefore the exceeding amount of water pushes the equilibrium totally to the right. Moreover the lignin dissolves, so the product is continuously removed. This is validated by the book of Young (ref. 5).

The enthalpy of reaction of the hydrolysis reaction of lignin is estimated with the help of the reaction enthalpy of the hydrolysis of maltose (see appendix 4.3). The enthalpy of reaction of the hydrolysis depends in the following way upon temperature:

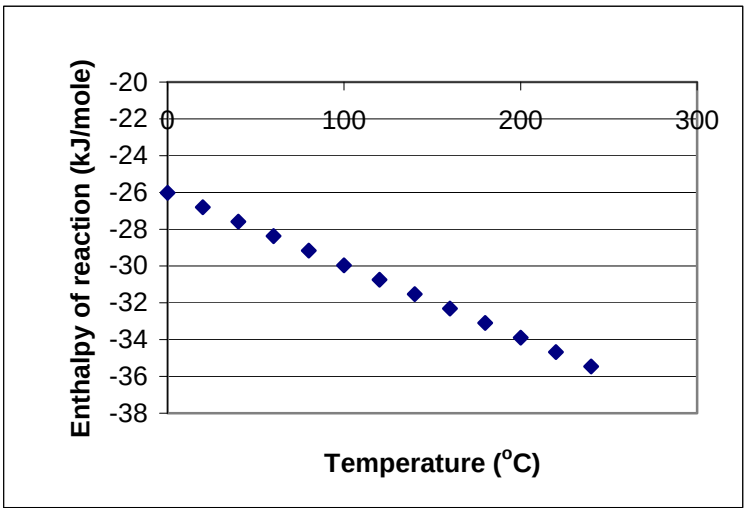


Figure 4.1: Dependence of enthalpy of reaction upon temperature

## 4.4.2 Bioconversion of monosaccharides to biogas and biomass

The stoichiometry of the overall reaction for the formation of biogas and biomass from the monosaccharides was made first (see appendix 4.3). The overall reaction equation is (on molar basis):

$$-1.0385\ C_6H_{12}O_6 + 1\ CH_{1.8}O_{0.5}N_{0.2} + 0.45\ H_2O - 0.20\ NH_4^+ + 0.20\ H^+ + 2.6405\ CO_2 + 2.5905\ CH_4 \qquad (4.3)$$

To calculate the volume of the fermentor the specific growth rate of the biomass is necessary. The specific growth rate of biomass can be calculated using the Monod relation:

$$\mu = \mu^{\max} \frac{C_s - C_{s,\min}}{C_s + K_s} \qquad (4.4)$$

with (ref. 59):

$\mu^{max}$ = 0.0125 $h^{-1}$

$K_s$ = 0.016 g/l

$C_{s,min}$ ≅ 0 g/l

This gives the following plot for the growth rate as function of the substrate concentration

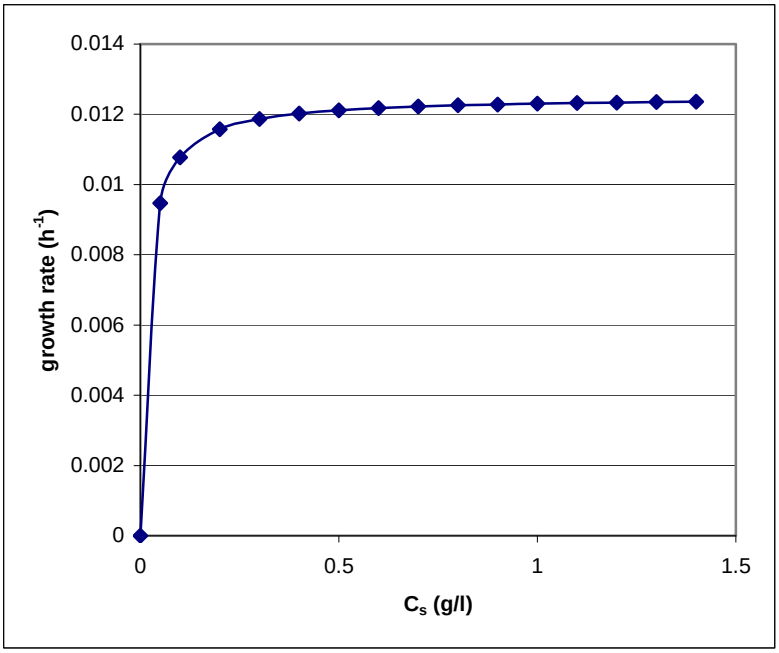


Figure 4.2: Monod kinetics for biomass formation (ref. 59)

The reaction enthalpy can be determined with the enthalpies of formation of the reactants and products in the overall reaction equation (see appendix 4.3). At 25 °C the enthalpy of reaction is –4407 kJ/kg biomass. Although our fermentation takes place at 40 °C, we will assume that the enthalpy of reaction is the same at 40 °C, because the temperature difference is relatively low.

## *4.5 Data accuracy*

The thermodynamic properties of willow wood were the most difficult to find or to estimate, as one cannot validate these data with experimental values. Nobody has ever measured the specific heat and enthalpy of formation of willow wood at different temperatures, and this wouldn't be meaningful either, because the composition of willow wood and the properties differ for each tree, in each environment and in each period of the year. Therefore it is impossible to say how accurate the thermodynamic data for willow wood are.

The estimated thermodynamic properties of willow wood were therefore validated using common sense. For example, it is logical that lignin with a lower molar weight can be dissolved in methanol more easily than lignin with a higher molar weight. Furthermore it is reasonable that very large molecules will stay dissolved in the liquid phase and not evaporate together with the solvent in the flashes.

Although it is impossible to determine the accuracy of the thermodynamic data for willow wood, it is possible to determine which properties are most important to know. The properties with the largest influence on the design are most sensitive to errors. The enthalpy of formation of willow wood only has effect on the calculated enthalpy of lignin and pulp, which have the same uncertainty in determining thermodynamic properties as the willow wood itself. The specific heat capacity of willow wood has only a minor influence on the amount of energy needed and produced in the design, because this is almost fully determined by the heats of evaporation of water and methanol.

More sensitive for errors is the solubility of lignin, which determines the amount of solvent needed, and thus the amount of energy needed to heat and compress the solvent. Also sensitive are the kinetics, which determine the residence time in the extractor and the volume of the extractor.

The kinetics will have to be tested on a smaller scale before it is possible to truly implement them on industrial scale. In the literature only few experimental data about the kinetics in the Alcell process were found. The information found in most cases was the measurement of conversion at a specific temperature and residence time. This information is most of the time the first thing to measure, but a better understanding of the kinetics would lead to a better design. Moreover unexpected problems can be prevented.

# 5 Process Structure & Description

In this chapter the block scheme from chapter 2 will be converted to a process flow scheme (PFS). This will be done by assigning equipment to the various blocks in the block scheme. After a certain piece of equipment is chosen for an operation, its operating conditions will be determined. The sizing and further calculation of the various pieces of equipment will be done in chapter 8.

## *5.1 Pretreatment*

The block scheme in chapter 2 starts with a block called pretreatment.
Pretreatment of the wood can be done to remove certain components of the wood in advance, which can facilitate the extraction and the recovery of by-products in later steps. Moreover pretreatment can also be applied to decrease the size of the wood chips, which decreases the time in the extraction. This can have big influence on the pulp quality, because shorter residence times of the wood chip in the extractor mean smaller degradation of the cellulose polymers. Also shorter residence times lead to energy savings.

Pretreatment methods can be grouped in 4 categories: physical, chemical, biological and a combination of these methods. Chemical pretreatment, i.e. the treatment of wood chips with chemicals such as hydrochloric acid and sulphuric acid to degrade and dissolve away the lignin and leave behind most of the cellulose, is not considered. Chemical pretreatment is not environmentally friendly, it degrades the cellulose and it involves the recovery of the (expensive) chemical.

The following pretreatment steps are considered:

- No pretreatment
- Steam explosion (combination of physical and chemical)
- Chipping (physical)
- Fungi (biological)

To choose the best option for pretreatment of the wood chips the following selection criteria are analyzed:

- *Duration of the pretreatment*: the pretreatment step should be as short as possible. If the pretreatment step is the slowest step in the process, the rest of the process is dependent on this step.
- *Investment costs*: the investments costs have influence on the economical feasibility of the plant. The smaller the investment costs, the more economically feasible the plant will be.
- *Pulp quality*: the quality of the wood chips after the pretreatment step has a big influence on the final pulp quality after the extraction.
- *Energy costs*: the energy costs of the equipment should be as low as possible to decrease the costs.
- *Safety*: the used pretreatment method should be as safe as possible, to decrease hazards to the employees, neighborhood and the environment.
- *Proven technology*: The pretreatment step should use proven technology as much as possible to insure safety and reduce (cost) risks.

- *Environment*: the process should be environmentally friendly. Toxic emissions should be kept within certain limits.
- *Complexity*: The process should be as simple and robust as possible, to reduce the investment costs and to ensure reliability

Now for each option the various selection criteria are evaluated. A short description of each option is given in appendix 5.1.

5.1.3 No pretreatment

The willow wood chips are sent to the reactor without any pretreatment. This means that size of the chips entering the extractor is relatively large (3x3x1 cm), which increases the extraction time in the reaction. Due to the large sizes of the chips, the diffusion distances of the solvent in the chips are large. Therefore during the extraction the penetration of solvent into the wood is the rate-determining step. This results in very long residence times in the extractor.

5.1.2 Steam explosion

*Duration of the pretreatment:* The steam explosion takes about 2-10 minutes.
*Investment costs:* Relatively large, the investment costs depend on the mode of steam explosion: batch or continuous. A continuous reactor is equipped with special feeding and discharge valves, which increases the investment costs.
*Pulp quality:* Steam explosion leads to a strong decrease in molar weight of the cellulose and therefore decreases the pulp quality.
*Energy costs:* Relatively large, steam explosion uses high-pressure steam, which is typically 15 – 30 bara and 180 – 210$^{o}$C.
*Safety:* This step is relatively unsafe, due to the large steam pressure used to generate an 'explosion'.
*Proven technology:* Yes, steam explosion is a commonly used process.
*Environment:* The process is environmentally friendly; no harmful compounds are used.
*Complexity:* The process is not very complex.

5.1.3 Chipping

*Duration time:* Relatively short. Chippers can have a large throughput, or more chippers in parallel can be used.
*Investment costs:* Relatively high.
*Pulp quality:* If the wood chips are not chipped too short, the cellulose polymers are hardly altered in length.
*Energy costs:* Relatively high, due to the formation of large amounts of heat, caused by friction. Moreover the efficiency of chipping is not very high, because steam (the main power source in the process) first has to be converted to electricity, which will drive the chipper.
*Safety:* Relatively safe. The chipping does take place with knifes, so care must be taken during the chipping.
*Proven technology:* Yes, chippers are widely used in the pulp and paper industry. Moreover they are commercially sold.
*Environment:* Chippers are environmentally friendly.

*Complexity:* Chippers are not complex. The wood chips are mechanically cut in smaller pieces with knifes.

### 5.1.4 Fungi

*Duration of the pretreatment:* The duration of the pretreatment with white rot fungi, varies from 1 to 4 weeks.
*Investment costs:* High, the wood chips must undergo several preliminary treatment steps, before they can be exposed to the fungi. Moreover, the fungi only grow when the conditions (temperature, humidity, moisture and nutrients content) are suitable. This requires the installation of extra equipment.
*Pulp quality:* The fungi only degrade the lignin in the wood chips. The cellulose polymers are not altered, which results in a better pulp quality.
*Energy costs:* The fungi only grow if the conditions are suitable. Energy must be supplied in the form of heat.
*Safety:* The degradation of lignin by white rot fungi is very safe.
*Proven technology:* Pretreatment with fungi is not a proven technology. There are still many uncertainties about the mechanism of lignin degradation by fungi, which prevents its commercial application.
*Environment:* The process is environmentally friendly; no harmful compounds are used or produced.
*Complexity:* The process is very complex. There are many variables that must be taken into account.

In the following table a summary of the weak and strong points of the different options is given.

Table 5.1: Comparison of the different options.

| | *Steam explosion* | *Chipping* | *Fungi* |
|---|---|---|---|
| Duration of the pretreatment | ++ | + | -- |
| Investment costs | +/- | - | - |
| Pulp quality | - | - | ++ |
| Energy costs | +/- | -- | +/- |
| Safety | +/- | +/- | ++ |
| Proven technology | + | + | -- |
| Environment | +/- | +/- | +/- |
| Complexity | + | + | -- |

The fungi option is rejected because of the large time required. Time wouldn't be a problem is the fungi could operate under normal conditions, so in the wood storage, but since special reaction conditions are required, this really is a limiting factor.
The chipping option is rejected because of the energy intensity and inefficiency of this process. Steam is used as power input. This steam would first have to be converted into electricity, which would than drive the chipper, in which a lot of heat is formed. This combined with a production of 100 kton/a of pulp makes a huge energy requirement.
This leaves the steam explosion as the best option for pretreatment.

## *5.2 Extraction*

The next block in the block scheme is the extraction stage. It is already been decided in chapter 2 to use an alcohol-water mixture for the extraction. Furthermore the decision is made to perform the extraction operation in a continuous mode of operation. This selection is further outlined in appendix 2.1.

## *5.3 Solvent Recovery – first step*

The next section is the solvent recovery. The stream entering this section is that out of the extractor. This stream's main components are solid cellulose and the solvent with dissolved lignin and hemicellulose. The first step now is to separate the cellulose from the solvent. This is a solid liquid separation. To separate the methanol-water solution from the pulp a pressurized device is needed. The stream that exits the extractor enters the solid-liquid separation device. This stream has a temperature of 190 °C and a pressure of 30 bara. Therefore it is important that the separation device works at a pressure of 30 bara to make sure that the methanol and water don't flash. Lower temperatures of the pulp stream will lead to lower pressures, because the saturated vapor pressures decrease with temperature. However the solubility of lignin strongly decreases with temperature. Therefore a decrease in temperature will lead to precipitation of the lignin in the pulp. Separation of the lignin from the pulp will then not be possible and pulp with a high lignin content that doesn't meet the requirements is the result.
There are several possibilities to separate solvent from the pulp. We have thought about devices that can work continuously without the need for regular stops for maintenance. We came up with the following 4 devices:

- Hydrocyclone
- Rotary Drum Filter
- Centrifuge
- Screw Press

For these 4 devices the following selection criteria are considered:

- *Efficiency of the separation:* The solvent must be separated as much as possible from the pulp. Insufficient removal will lead to a high methanol content in the pulp and lower pulp quality.
- *Pressure:* Is it possible to operate the device at a pressure of at least 30 bar
- *Proven technology:* The process should use proven technology as much as possible to insure safety and reduce (cost) risks.
- *Costs*: High purchase prices will lead to higher investment costs
- *Power requirement:* Higher power requirements lead to an increase in the variable costs
- *Capacity:* Is the capacity of the device sufficient enough to process the pulp. If the capacity of the device is not sufficient enough several devices have to be placed in parallel.
- *Complexity:* The process should be as simple and robust as possible, to reduce the investment costs and to ensure reliability

Now for each of the 4 options the selection criteria are evaluated. A short description of each option is given in appendix 5.2.

### 5.3.1 Hydrocyclone

*Efficiency of the separation:* Due to the small density difference between wood pulp and the solvent (about 50 kg/m$^3$), efficient separation will not be achieved. The pulp that exits the hydrocyclone will contain too much solvent.
*Pressure:* It is possible to operate a hydrocyclone at 30 bara. However the pressure drop over the hydrocyclone may not be to high, because else the methanol and water will flash.
*Proven technology:* Yes, hydrocyclones are extensively used in industry.
*Costs*: Hydrocyclones are relatively simple devices with relatively low purchase costs.
*Power requirement:* No power consumption, the centrifugal force is generated by the liquid motion.
*Capacity:* The hydrocyclone diameter may not be too big at high pressure. It is difficult to keep a big apparatus under pressure. At smaller diameters the capacity of the hydrocyclone decreases and several hydrocyclones have to be placed in parallel.
*Complexity:* A hydrocyclone is a simple device.

### 5.3.2 Rotary Drum Filter

*Efficiency of the separation*: A rotary drum filter is very effective in separating the pulp from the solvent. The solvent passes through the filter and the pulp stays behind and forms a cake on the filter.
*Pressure:* It is possible to operate a rotary drum filter at 30 bara. However the drum filter must be placed in a vessel to keep the pressure at 30 bara round the drum, which could be very costly. Moreover the pressure drop over the filter may not be too high, to prevent flashing of the solvent
*Proven technology:* Rotary drum filters are frequently used in industry, however not at pressures over 15 bara.
*Costs*: Rotary drum filters are very expensive devices.
*Power requirement:* Relatively high, due to rotation of the drum.
*Capacity:* High, a drum filter can handle large throughputs.
*Complexity*: High, due to the high pressure at which the drum filter is operated

### 5.3.3 Centrifuge

*Efficiency of the separation*: Due to the small density difference between wood pulp and the solvent (about 50 kg/m$^3$), efficient separation will not be achieved.
*Pressure:* It is possible to operate a centrifuge at 30 bar.
*Proven technology:* Yes, centrifuges are extensively used in industry.
*Costs*: Centrifuges are relatively simple devices with low purchase costs.
*Power requirement:* The centrifugal force is generated by rotation of the device. Therefore the power requirement is relatively high.
*Capacity:* The hydrocyclone diameter may not be too big at high pressure. It is difficult to keep a big apparatus under pressure. At smaller diameters the capacity of the hydrocyclone decreases and several hydrocyclones have to be placed in parallel
*Complexity*: A centrifuge is a relatively simple device.

### 5.3.4 Screw Press

*Efficiency of the separation*: A screw press is an efficient device to separate the solvent from the pulp. Filtrate is removed through the perforated cage and the solids are discharged at the end of the press.
*Pressure:* The pulp is compressed to high pressures, while the filtrate is discharged at high pressures.
*Proven technology:* Yes, screw presses are extensively used in the pulp and paper industry.
*Costs*: A screw press is an expensive device.
*Power requirement:* Relatively high due to the rotation of the screw
*Capacity:* The screw press can handle relatively large throughputs.
*Complexity*: A screw press is a relatively simple device.

The selection criteria for the 4 devices are summarized in the following table:

Table 5.2: Summary of the selection criteria

| | *Hydrocyclone* | *Rotary Drum Filter* | *Centrifuge* | *Screw Press* |
|---|---|---|---|---|
| Efficiency of the separation | -- | + | -- | + |
| Pressure | + | - | + | + |
| Proven Technology | + | - | + | + |
| Costs | + | - | + | - |
| Power requirements | ++ | - | - | - |
| Capacity | +/- | + | - | + |
| Complexity | + | - | - | + |

After looking at the table, the hydrocyclone and the screw press have the most positive factors. However the efficiency of the separation is a very important factor. The hydrocyclone will not achieve an effective separation of the solvent from the pulp due to the small density difference. Therefore we have decided to choose a screw press for the separation of the solvent from the pulp, although the power requirements and purchase costs are higher.

## *5.4 Solvent Recovery – second step*

Now the solvent and pulp are separated. The pulp can go to the pulp screening and drying block, but the solvent isn't ready to go back to the extraction section yet. The solvent still contains lignin and hemicellulose, which are dissolved in the solvent. The solvent has to be free of these substances, before it can be returned to the extractor.
Because the solvent flowing back to the extractor has to be rich in methanol, part of the solvent recovery has to be some kind of flash or distillation. Furthermore the lignin will be used as fuel, so it must be a solid and not be in solution, so some kind of precipitator has to be used to separate the lignin. Using these criteria, three main options are generated:

- Use three pieces of equipment: first flash off a large part of the solvent in an adiabatic flash. Then separate the lignin using some kind of solid/liquid separator and finally lead the remaining fluid through a distillation column to create a methanol-rich phase, which can go back to the extractor and a water-rich phase, which can be treated further.

- Use two pieces of equipment: use a combination of a flash vessel and S/L separator to flash off part of the solvent and precipitate the lignin. Then use a distillation column to separate the remaining fluid in a methanol-rich phase, flowing back to the extractor, and a water-rich phase, which can be treated further.
- Use one apparatus: use a kind of distillation column, in which the reboiler functions as a S/L separator and in which the feed enters almost at the bottom of the column, to avoid precipitation of lignin in other parts of the column.

To select the best option a number of selection criteria is used:

- Recovery of solvent
- Recovery of lignin
- Complexity of installation
- Process costs
- Energy demand
- Proven technology
- Safety, health & environment

### 5.4.1 Option 1: 3 separate pieces of equipment

- *Recovery of solvent*: Because all three apparatuses can be tuned separately, the recovery of solvent can be very high.
- *Recovery of lignin*: Because the temperature and pressure in the S/L precipitator can be chosen more or less freely (but of course not deviating too much from that in the other equipment), the recovery of lignin can be very high.
- *Complexity of installation*: Complex, in the sense that separate equipment is used for every function, but the various pieces of equipment do not have to be very complex themselves.
- *Process costs*: High process costs because of complexity and (most likely) varying temperature and pressure in different pieces of equipment.
- *Energy demand*: High energy demand because of more pieces of equipment and (most likely) varying temperature and pressure between them.
- *Proven technology*: All the separate pieces of equipment are very common in chemical technology (flash vessel, S/L separator, distillation column).
- *Safety, health & environment*: A higher risk is caused by the high complexity of operation, but this can be compensated by the fact that these are all common apparatuses with well know safety issues.

### 5.4.2 Option 2: combined flash & S/L separator and separate distillation column

- *Recovery of solvent*: The separate distillation column can separate almost all solvent, remaining after the flash, back to the extractor, so a high recovery is possible.
- *Recovery of lignin*: The conditions in the combined flash & S/L separator cannot be chosen entirely freely; they have to satisfy both the conditions required for effective flashing and the conditions for effectively separating lignin, so this will inevitably create some kind of compromise, lessening the recovery of lignin.
- *Complexity of installation*: Compared to option 1, the number of apparatuses has diminished, making the operation less complex. On the other hand, the combined flash/separator is more complex than a single flash or S/L separator.

- *Process costs*: The installation is less complex and less energy demanding than option 1 and therefore has lower process costs.
- *Energy demand*: Combining flash and separator diminishes the energy demand of the process.
- *Proven technology*: The combination of flash and separator isn't normally used in chemical industry.
- *Safety, health & environment*: The reduced number of apparatuses also reduces the risks for safety, health and environment.

### 5.4.3 Option 3: One piece of equipment with all functions combined

- *Recovery of solvent*: Because the reboiler of the apparatus also serves as an S/L separator, it's not possible to choose the conditions in the column completely freely and therefore the recovery of solvent might not be as good as with a separate column.
- *Recovery of lignin*: Same arguments as under 'Recovery of solvent': recovery of lignin might not be as good as with a separate separator.
- *Complexity of installation*: Only 1 piece of equipment, so less complex than other two options in this sense, but the combined separator/column will be more complex than a single separator or column.
- *Process costs*: Only one piece of equipment, but this apparatus will cost more than a simple distillation column.
- *Energy demand*: Because all the steps are integrated, this option will have a lower energy demand than the other options.
- *Proven technology*: A combination of S/L separator and distillation column isn't normally used, so no proven technology at all.
- *Safety, health & environment*: All the material is maintained in one piece of equipment, reducing risk of leakage, and therefore reducing these risks.

The aforementioned selection criteria can be summarized using the +/- method. This is done in table 5.3.

Table 5.3: Summary of selection process

| *Selection criterion* | *Option 1* | *Option 2* | *Option 3* |
|---|---|---|---|
| Recovery of solvent | ++ | + | +/- |
| Recovery of lignin | ++ | + | +/- |
| Complexity of installation | + | +/- | - |
| Process costs | - | +/- | +/- |
| Energy demand | - | +/- | + |
| Proven technology | ++ | - | -- |
| Safety, health & environment | +/- | +/- | + |

Based on table 5.3 we have decided for option 1. This is the most reliable and robust option, giving the highest recoveries of both solvent and lignin.

### 5.4.4 Equipment selection

Now equipment has to be selected for the three functions mentioned.
For the flash operation, a simple flash tank can be used, with the modification that the lignin slurry can be withdrawn from the bottom. The stream coming from the screw press enters the flash at high pressure and temperature. In the flash tank the solvent is

adiabatically flashed to atmospheric pressure. This will evaporate a large part of the solvent. Because the vapor phase can contain virtually no lignin or hemicellulose, the vapor stream coming from the flash can go back directly to the extractor, after condensation.
The stream leaving the bottom of the flash consists of solid lignin (lignin precipitates for 99.99%, see appendix 4.1 and appendix 8.6) and still a lot of solvent. Because of the drop in temperature, almost all lignin has been deposited and therefore the separation of lignin and solvent has now become a quite straightforward separation. The hemicellulose has a far higher solubility in water and almost all of the hemicellulose will still be in solution.
For the separation of lignin from an aqueous hemicellulose solution, the same devices are considered as for the separation of the solvent from the pulp. Also the same factors are considered, except for the factor pressure; the separation takes place at low pressure and low temperature.
The density of lignin is much larger than the density of the aqueous hemicellulose solution (1700 kg/m$^3$ for lignin versus ca. 1000 kg/m$^3$ for the aqueous hemicellulose solution). Therefore separation of the lignin from the aqueous solution is excellently possible with a hydrocyclone or centrifuge. The table 5.4 can now be made:

Table 5.4: Summary of the selection criteria

| | *Hydrocyclone* | *Rotary Drum Filter* | *Centrifuge* | *Screw Press* |
|---|---|---|---|---|
| Efficiency of the separation | + | + | + | + |
| Pressure | + | - | + | + |
| Proven Technology | + | - | + | + |
| Costs | + | - | + | - |
| Power requirements | ++ | - | - | - |
| Capacity | - | + | - | + |
| Complexity | + | - | - | + |

From table 5.4 it is clear that the hydrocyclone is the best option for the separation of the lignin from the aqueous hemicellulose solution.
The last of the three functions is some kind of distillation. Because methanol/water is a fairly easy separation, a simple column will do the job here.

## *5.5 Screening and drying of pulp*

During the pulping process not all of the wood will be sufficiently delignified. Especially the hard pieces from the wood are difficult to pulp. This is because the steam doesn't penetrate easily into these hard pieces and the explosion will not tear apart the knots. Moreover the extraction with an alcohol solvent is more difficult.
Screening of the pulp after pulping is a process whereby the pulp is separated from large shives, knots, dirt and other debris. This is important for improving the appearance and printability of paper. Moreover during screening the fibers can be fractionated by length. Screens separate particles on the basis of size. Accepts consist of the small pulp particles that passed through the screens. Rejects are the larger shives, knots, large dirt particles and other debris removed by the screens.
Many types of screens are available, but they all depend on some form of perforated barrier to pass acceptable fiber and reject the unwanted material. The size of the perforations determines the size of the particles that will be removed. For small particles woven cloth or wire screens are used, and for larger sizes, perforated metal plates or grids. In our case pulp is screened through small holes or slots in metal

plates to remove shives, dirt and other large particles. All screens must be equipped with some mechanism to continuously or intermittently clean the openings in the perforated barrier, for example vibration or rotation. Otherwise, the screen plate would rapidly plug up.
Therefore all screening equipment has two functions:

1. Give undersize material maximum opportunity to pass through the mesh openings, but without the loss of oversize material at the same time.
2. Prevent the material from lodging in the mesh openings.

The simplest industrial screening equipment are stationary screens, over which the material to be screened flows. Today stationary screens are hardly used anymore because they are not efficient. Dynamic screening equipment can be categorized according to the type of motion used to shake-up and transport the material on the screen.
The major types of dynamic screeners used in the pulp and paper industry are:

1. Vibratory (flat or rotary)
2. Gravity centrifugal
3. Pressure

A short description of these three types of screeners is given in appendix 5.3.

### 5.5.1 Comparison of the types of screens

In table 5.5 one can find the comparison between the different types of screeners. Selection criteria are the achieved separation, the capacity, required screening area, operating costs (maintenance, labor, pumping), foaming, proven technology, safety (enclosed screens are safer) and noise (enclosed screeners that don't vibrate are less loud). For our process the pressure screen seems to be the best option.

Table 5.5: Comparison of the types of screens

| *Property* | *Vibratory screen* | *Centrifugal screen* | *Pressure screen* |
|---|---|---|---|
| Separation | + | + | + |
| Capacity | -- | +/- | ++ |
| Screening area | -- | +/- | ++ |
| Operating costs | -- | + | +/- |
| Proven technology | + | + | + |
| Foaming problems | -- | +/- | +/- |
| Safety | - | + | +/- |
| Noise | -- | + | + |

### 5.5.2 Where to screen in our process

One could ask where to screen the pulp. It is namely possible to screen the pulp after the steam explosion or after the extraction.
If the particles aren't small enough after the steam explosion the penetration time in the extractor becomes too high and total extraction becomes impossible. If one screens the pulp directly after the steam explosion, the large particles can be sent back to the steam explosion to be pulped again. In this way the recycle stream flows through less equipment. The more energy demanding extraction process is carried out without the too large particles.
One could also screen the pulp after the extraction. This requires smaller holes (particles also become smaller in extraction), a larger pressure drop (smaller holes) and a recycle stream through more equipment.

We will choose to screen the pulp directly after the steam explosion, because then a smaller pressure drop is needed and the recycle stream flows through as few equipment as possible. This is one of the design heuristics according to Douglas (ref. 13).

### 5.5.3 Drying of pulp and lignin

The pulp coming from the screw press still contains quite a lot of solvent. The pulp leaving the process should have a moisture content of about 6% by volume, and therefore a large part of the remaining solvent has to be removed. As with the lignin, this can be done for a large part by a flash operation. This is also likely to be the most energy efficient way, because the pressure and temperature of the stream is used to achieve separation in the flash. Because the vapor phase can hardly contain any cellulose, the vapor stream leaving the flash can be recycled directly to the extraction section.
By having a closer look at the consistency of cellulose pulp (i.e. by looking at pictures and feeling the pulp ourselves at Norske Skog Parenco B.V. (see appendix 12.2), it quickly became clear that this material is not suitable for the solid/liquid separations, as mentioned under paragraph 5.3. Therefore we decided to leave out this operation and send the pulp from the flash directly to a dryer.
In our process drying is performed at two places. Not only the cellulose pulp has to be dried to a certain moisture content, but the stream of lignin that leaves the hydrocyclone with the underflow also contains large amounts of water and methanol. The presence of water in the lignin considerably decreases the heat of combustion of the lignin and should therefore be removed.
The methanol and the water should not only be removed from the pulp and the lignin, but the methanol should also be recovered. The evaporated methanol and water should therefore be collected at the end of the dryer and consequently condensed to fluid methanol and water. Then the methanol and water can be used again in the extractor.
There are several options to supply heat for the separation process. The combustion gases from the lignin combustion can be used for directly heating the pulp and the lignin. However combustion gases contain large amounts of impurities that will pollute the pulp, methanol and water (lignin is burnt and impurities from the combustion gases in the lignin are therefore not important). This problem could be solved by using a hot clean air stream or by indirect heating of the pulp or lignin with the combustion gases. The hot combustion gases are then led through heating tubes. Another disadvantage of the use a hot gas stream is the low heat capacity of gas. For the heating and evaporation of water and methanol an extremely large gas stream would be needed.
A better option is the use of saturated steam. The steam can be led through tubes and by condensation of the steam a large amount of heat is released. The lignin is thus heated indirectly. The liberated heat is used for heating and evaporation of methanol and water. An advantage of the use of steam is the high heat of condensation that is liberated in the dryer. Therefore the application of steam will lead to considerably smaller streams through the dryer, compared to the use of gas. Moreover in the process low-pressure ‘waste’ steam is generated during the steam explosion that could perfectly be used.

During the steam explosion low-pressure steam is generated of 115 °C and 1.7 bara (see chapter 8). A part of this steam is used for preheating of the wood chips. The other part could be used for the drying of lignin and pulp. The liquid with the highest boiling point is water. The lignin and pulp have to be heated to maximally 100 °C to remove the water and the methanol. The steam condenses at 115 °C and therefore the temperature difference, which is the driving force for heat transfer, is always high enough. Therefore the low-pressure steam is suitable to supply heat for the evaporation process.
Rotary steam tube dryers are frequently used in industry for continuous processes when indirect heating with steam takes place. A rotary steam tube dryer is a rotating cylinder, containing rows of steam tubes arranged in concentric circles, and extending the full length of the cylinder. The tubes are fastened symmetrically in one, two or three rows inside the cylinder. When handling sticky materials, one row of tubes is preferred. Lifting flights are usually inserted behind the tubes to promote solids agitation.
Saturated steam flows counter-currently to the pulp mixture through the tubes to increase the heat transfer between the steam and the lignin or the pulp.
The thermal efficiency of the dryer is very high and heat loss through the cylinder wall is minimal, because the steam tubes are completely enclosed by the dryer.
A low air velocity through the dryer is required to remove the vapors and to promote the evaporation process.
For the drying process a rotary steam tube dryer is chosen with stainless steel tubes, which are fastened in one row at the inside of the cylinder. The heat source is saturated steam of 115 ° and 1.7 bara.

### *5.6 Byproducts formation and recovery*

The last block is now the one where the remaining streams are converted to useful products. The streams entering this block are those coming from the solvent recovery section. The stream of lignin with solvent is sent to a dryer, as described in section 5.5.3. The lignin leaving the dryer requires no further treatment and can be sent directly to a furnace to be burnt.
The other stream entering this block is an aqueous stream containing water, some methanol and hemicellulose. The choice has been made earlier on to produce biogas from this stream. The only feasible way to achieve this is by anaerobic digestion of this aqueous stream. Biogas can be produced from an aqueous stream containing hemicellulose by different types of bacteria. During the fermentation in an anaerobic digester the hemicellulose is hydrolysed, converted to organic acids and further converted to methane and carbon dioxide. The produced biogas consists mainly of methane (50 mole%) and carbon dioxide (50 mole%), but also contains trace levels of other gases such as hydrogen, carbon monoxide, nitrogen, oxygen, and hydrogen sulphide.
The equipment needed for this type of operation is an anaerobic digester.

### *5.7 Flowsheet description*

Now that all equipment has been selected, a flowsheet (PFD) can be made. This PFD can be found in appendix 5.7. The PFD will now be explained step by step. First the route of the main product (cellulose pulp) through the process will be followed.

### 5.7.1 Conveyor (X01)

The wood chips coming from the wood storage facility have to be transported to the first step in the process; the presteaming section (X02). For this a conveyor belt is used (X01).

### 5.7.2 Presteaming (X02)

The wood chips <1> coming from the wood storage facility first enter the presteaming section (X02) via a conveyor (X01). This section is part of the steam explosion. In the presteaming section the wood chips are treated with low-pressure steam coming from the flash in the steam explosion (V01). The function of presteaming is to let the low-pressure steam penetrate in the wood before it enters the steam explosion itself. The flash in the steam explosion flashes to 1.7 bar, so this is also the pressure of the steam entering the presteam. The stream coming out of the presteam <3> will go to the heating section (X02) of the steam explosion.

### 5.7.3 Steam Heating (X03)

In the steam heating section (X03) high-pressure steam <2> is added to the wood chips. This high-pressure steam condenses on the wood chips and than diffuses into the pores of the wood. The steam entering this section has a pressure of 12.6 bara and a temperature of 190 °C. The steam heating section (X03) consists of a tubular reactor with a rotating screw to transport and compress the wood mass. At the end of this tube the steam has penetrated deep into the wood and the stream leaving this section <4> goes to the explosion (flash) section (V01). In reality this section consists of two apparatuses to achieve the right throughput, but for simplicity only one is depicted in the PFS.

### 5.7.4 Flash / Explosion (V01)

The stream of wood chips penetrated with water <4> now enters the explosion section (V01), where the pressure is instantly lowered from 12.6 to 1.7 bara. This causes a large part of the water to evaporate again, thereby tearing apart the structure of the wood. The vapor phase <6> is partly recycled <5> to the presteaming section (X02). The rest <7> is used elsewhere in the process for a drying operation. The wood, which has now become pulp <8>, is than sent to the screener (S01).

### 5.7.5 Cooler (E01)

Before going to the screen, the pulp <8> has to be cooled. This is because there is a small pressure drop over the screener. If <8> wouldn't be cooled, this pressure drop would result in the formation of vapor in the screener. By cooling, this phenomenon is avoided.

### 5.7.6 Screener (S01)

The pulp coming from the steam explosion <8> has to be screened for any pieces of wood that haven't been pulped properly in the steam explosion. In the screener these pieces, called rejects, are separated by size from the rest of the pulp. The rejects <10>

are partly sent back to the steam heating section (X03) of the steam explosion <11> and partly purged <12> to prevent build-up. The screened pulp <9> can now be sent to the extractor (R01).

### 5.7.7 Conveyor (X04)

The stream <9> coming from the screener (S01) has to be transported to the extractor (R01). For this goal a conveyor (X04) is used.

### 5.7.8 Preheater (E02)

When <9> enters the extractor (R01), this stream has to be brought up to reactor pressure (33 bara) and temperature (190 °C). The mixture has to be brought up to pressure first to avoid formation of vapors. This is done by compressing <9> in the feeder of the extractor (R01). Bringing <9> up to temperature is done with preheater (E02). The pressurizing and heating are actually done simultaneously in the extractor (R01) feeder. For clarity and a clear understanding of the heat balance the preheater (E02) is depicted in front of the extractor (R01) in the PFS.

### 5.7.9 Extractor (R01)

As stated before the pulp feed <9> to the extractor is pressurized and heated in the feeder of the extractor (R01). After the feeder the solvent <13> is added. The solvent is already brought up to pressure (33 bara) and temperature (190 °C) by respectively the solvent feed pump (P01) and solvent feed heater (E03). Here again, <13> is first pressurized and heated thereafter, to avoid formation of vapors. The pulp and solvent then enter the screw of the extractor (R01), and flow cocurrently through the screw, by rotation of the screw. At the end of the screw the lignin is sufficiently extracted and the stream <14> leaving the extractor (R01) can be separated into a pulp stream and a solvent stream in the screw press (X05).

### 5.7.10 Screw Press (X05)

The stream <14> coming from the extractor (R01) has to be separated in a pulp stream <15> and a solvent stream <18>, containing the lignin. This is done in the screw press (X05). The screw presses the solvent out of the pulp. To avoid precipitation of lignin in the pulp, the temperature and pressure have to be the same as in the extractor (R01), respectively 190 °C and 33 bara.

### 5.7.11 Flash Vessel (V02)

In order to further dry the pulp <15> coming from the screw press (X05), a flash operation is performed, where the pressure is lowered from 33 bara to 1 bar. This is done in a simple flash vessel (V02). The vapor phase <19> coming from the flash vessel (V02) contains only water and methanol and can therefore be recycled directly to the extractor (R01). To achieve this <19> is sent to a mixer (M01) where it is mixed with the recycle stream <20> from another flash (V03) and with the make-up streams for water <40> coming from the water storage tank (T01) and methanol <17> coming from the methanol storage tank (T02). The bottom stream <16> coming from

the flash vessel (V02), containing the pulp has to be dried even further to achieve product specifications and is therefore sent to the cellulose dryer (D01).

### 5.7.12 Dryer (D01)

The cellulose pulp <16> coming from the flash vessel (V02) is dried further in the cellulose dryer (D01) by adding heat. This heat is supplied by low pressure steam which partly <7> comes from the flash (V01) in the steam explosion. The steam flows through steel tubes and condensates there. The pulp is led over the outside of the tubes. The solid stream <32> coming out of the dryer (D01) is the end product. The vapor stream <31> coming out of the dryer contains a relatively high amount of water and therefore has to be treated further, before being sent back to the mixer. This stream <31> is sent to a mixer (M02) to be mixed with other streams, before entering a distillation column.

Besides the route of the main product, cellulose pulp, the rest of the process will now be described. In this part of the process the solvent is recovered and the byproducts are formed.

### 5.7.13 Flash Vessel (V03)

The solvent stream <18> coming from the screw press (X05) contains a lot of lignin and hemicellulose. This lignin and hemicellulose has to be separated from the solvent, before the solvent is recycled to the extractor (R01). The lignin is precipitated in a flash vessel (V03). In this vessel the pressure is lowered to 1 bar, thereby causing the evaporation of a large part of the solvent. The vapor <20> coming from the flash vessel (V03) can hardly contain any lignin and can therefore be recycled directly to the extractor (R01). The bottom stream <21> coming from the flash vessel (V03) is a slurry containing the lignin and still a considerable amount of solvent. The solvent contains the hemicellulose. The solvent is partly recovered in a hydrocyclone (S02).

### 5.7.14 Pump (P05)

The bottom stream <21> coming from the flash vessel (V03) has to have a certain speed when entering the hydrocyclone (S02), in order to achieve separation. This is done by building up some pressure, which is lost again in the form of pressure drop over the hydrocyclone (S02). This pressure is built up in the hydrocyclone feed pump (P05).

### 5.7.15 Hydrocyclone (S02)

The slurry <21> coming from the flash vessel (V03) still contains a lot of solvent. This is partly recovered in the hydrocyclone (S02). The bottom stream <23> of the hydrocyclone (S02) still contains a small amount of solvent, which is recovered in a dryer (D02). The top stream <22> of the hydrocyclone (S02) consists of solvent with hemicellulose and a small amount of lignin. This stream <22> cannot be recycled directly to the extractor (R01), due to the presence of hemicellulose.

5.7.16 Dryer (D02)

The bottom stream <23> coming from the hydrocyclone (S02) still contains a small amount of solvent, which is removed by drying. The type of dryer used here is the same as for the cellulose dryer (D01). The heat required for drying comes from low-pressure steam, which partly <7> comes from the flash vessel (V01) in the steam explosion. After drying the lignin <24> is dry enough to be burnt in the furnace. The vapor stream <30> coming from the dryer contains a relatively large amount of water and is therefore sent to the same mixer (M02) as the stream <31> from the cellulose dryer (D01), to be treated in a distillation column.

5.7.17 Condenser (E08)

The vapor stream <31> coming from the cellulose dryer (D01) has to be condensed before being sent to the sieve tray column (C01). This is done in the D01 condenser (E08).

5.7.18 Pump (P07)

The stream <31> coming from the cellulose dryer (D01) has to be transported to the C01 feed mixer (M02). This is done by the to C01 feed mixer pump (P07).

5.7.19 Mixer (M02)

The streams <31> and <30> coming from the cellulose dryer (D01) and lignin dryer (D02) and the stream <22> coming from the top of the hydrocyclone are mixed in the C01 feed mixer (M02). These streams have to be mixed before entering the sieve tray column (C01). The output <33> of the C01 feed mixer (M02) flows to the sieve tray column (C01).

5.7.20 Condenser (E07)

The vapor stream <30> coming from the lignin dryer (D01) has to be condensed before being sent to the sieve tray column (C01). This is done in the D02 condenser (E07).

5.7.21 Pump (P06)

The stream <30> coming from the lignin dryer (D02) has to be transported to the C01 feed mixer (M02). This is done by the to C01 feed mixer pump (P06).

5.7.22 Condenser (E04)

The stream <19> coming from the cellulose flash vessel (V02) has to be condensed before it can be transported and mixed in the solvent feed mixer (M01). This is done in the condenser V02 (E04).

5.7.23 Pump (P03)

The stream <19> coming from the cellulose flash vessel (V02) has to be transported to the solvent feed mixer (M01). This is done by the to solvent feed mixer pump (P03).

5.7.24 Condenser (E05)

The stream <20> coming from the lignin flash vessel (V03) has to be condensed before it can be transported and mixed in the solvent feed mixer (M01). This is done in the condenser V03 (E05).

5.7.25 Pump (P04)

The stream <20> coming from the lignin flash vessel (V03) has to be transported to the solvent feed mixer (M01). This is done by the to solvent feed mixer pump (P04).

5.7.26 Pump (P09)

The make-up water stream <40> coming from the water storage tank (T01) has to be transported to the solvent feed mixer (M01). This is done by the water feed pump (P09).

5.7.27 Pump (P02)

The make-up methanol stream <17> coming from the methanol storage tank (T02) has to be transported to the solvent feed mixer (M01). This is done by the methanol feed pump (P02).

5.7.28 Mixer (M01)

The streams <19> and <20> coming from the cellulose flash vessel (V02) and lignin flash vessel (V03), the stream <25> returning from the reflux accumulator (V05) and the make-up streams for water <40> and methanol <17> have to be mixed before entering the extractor (R01). This is done in the solvent feed mixer (M01).

5.7.29 Pump (P01)

The solvent stream <13> leaving the solvent feed mixer (M01) has to be brought up to the pressure (33 bara) and temperature (190 °C) in the extractor (R01). The solvent feed pump (P01) pressurizes stream <13> to 33 bara.

5.7.30 Heater (E03)

The solvent stream <13> leaving the solvent feed mixer (M01) has to be brought up to the pressure (33 bara) and temperature (190 °C) in the extractor (R01). The solvent feed heater (E03) heats stream <13> to 190 °C.

5.7.31 Pump (P08)

The stream <33> coming from the C01 feed mixer (M02) has to be transported to the sieve tray column (C01). This is done by the C01 feed pump (P08).

5.7.32 Sieve Tray Column (C01)

Stream <33>, containing water, methanol and hemicellulose has to be separated in a water-rich <35> and a methanol-rich <34> phase. The water-rich phase will be collected at the bottom of the column (C01) (water has a higher boiling point then methanol) and because hemicellulose dissolves mostly in water and barely in methanol the hemicellulose will leave the column with the bottom stream <35>.

5.7.33 Reboiler / Condenser (E09)

Because the duties of the reboiler and condenser of the sieve tray column (C01) are very high, the choice was made to exchange heat between the top stream <34> and bottom stream <35>. This is done in the combined reboiler / condenser (E09). Part of the top stream <34> condenses, thereby freeing heat with which part of the bottom stream <35> is evaporated.

5.7.34 Compressor (K01)

As said before heat will be exchanged between the bottom <35> and top stream <34>. The top stream <34> has to be cooled with the bottom stream <35> and the bottom stream <35> has to be heated with the top stream <34>. Problem here is that the bottom stream <35> has a higher temperature than the top stream <34>, so it is impossible to transport heat in the desired direction. Some kind of energy input is needed, and this is acquired by the overhead compressor (K01). This piece of equipment compresses the gas stream <34> from the top of the column (C01), thereby raising the temperature of <34>. Now heat exchange in the combined reboiler / condenser (E09) is possible.

5.7.35 Condenser (E10)

After the reboiler / condenser (E09) part of the top stream <34> is vapor and the rest liquid. Because the stream going back into the top of the column (C01) has to be liquid, the vapor in stream <34> has to be condensed. This is done in the C01 condenser (E10).

5.7.36 Reflux Accumulator (V05)

Part of the top stream <34> has to be recycled <37> to the top of the column (C01) and part is taken as the distillate <25>, which is sent to the solvent feed mixer (M01). The ratio between these streams is determined by the desired reflux ratio of the column (C01). The split in these two streams is achieved in the reflux accumulator (V05).

5.7.37 L/V Phase Splitter (V06)

After the reboiler / condenser (E09) part of the bottom stream <35> has been evaporated and another part is still liquid. The vapor phase <36> will be sent back into the column (C01) and the liquid phase <26>, containing the hemicellulose, will be sent to the fermentor (V04) for further treatment. The phase split between vapor <36> and liquid <26> phase is achieved in the L/V Phase Splitter (V06).

5.7.38 Cooler (E06)

When stream <26> leaves the phase splitter (V06) the temperature will be about the boiling temperature of water at atmospheric pressure (~100 °C). The microorganisms in the fermentor can't handle this temperature and therefore stream <26> is cooled to about 40 °C in the fermentor feed cooler (E06).

5.7.39 Anaerobic Fermentor (V04)

The stream <26> coming from the column (C01) still contains hemicellulose. This hemicellulose is converted to biogas in the fermentor (V04). Actually 4 fermentor vessels are needed, but only one is shown on the PFS for simplicity. The streams leaving the fermentor are biogas <27>, biomass <29> and wastewater <28>. The wastewater is partly recycled to the fermentor <39> and partly sent to the fields <38> where the willow trees grow, to serve as fertilizer. This stream <38> namely holds the unconverted minerals.

5.7.40 Pump (P10)

The wastewater stream <39> recycled to the fermentor (V04) has to be transported. This is done by the fermentor recycle pump (P10).

5.7.41 Cooler (E11)

The wastewater stream <39> recycled to the fermentor (V04) is cooled, to remove the heat produced by reactions in the fermentor (V04). This cooling takes place in the fermentor recycle cooler (E11).

5.7.42 Storage Tank (T01)

To ensure continuous operation a certain amount of process water should be kept in storage. This water is used as make-up water <40> and boiler feed water (BFW). It is kept in the water storage tank (T01).

5.7.43 Storage Tank (T02)

To ensure continuous operation a certain amount of methanol should be kept in storage. This methanol is used as make-up methanol <17>. It is kept in the methanol storage tank (T02).

5.7.44 Cooling Tower (E12)

The cooling water (CW) used in the process has to be cooled down to a certain temperature before going back to the river. To cool down the water a cooling tower (E12) is used.

5.7.45 Furnace (F01)

The lignin <24> coming from the lignin dryer (D02) and part of the biogas <27> produced in the fermentor (V04) is burnt to produce energy. This is done in a fluidized bed furnace (F01)

## *5.8 Stream Summary*

The stream summary is given in appendix 5.4.

## *5.9 Utilities*

The assignment states that the process should be self-supporting in energy. For this reason there are no utilities crossing the battery limit, except cooling water (CW) and boiler feed water (BFW). The steam required is generated in a furnace by burning byproducts (lignin and biogas). The energy produced there is transferred to water to produce steam. To compensate for steam losses boiler feed water has to be added to the furnace as a utility. The electricity required is generated by expanding the steam from the furnace in a turbine.
A utility summary is given in appendix 5.5.
The cooling water required is pumped from the nearby river and when used it flows back to the river, after having been cooled down to a permitted temperature. There are little or no alternatives for this utility. If a better use were found for the (low quality) heat produced in the process, the need for cooling water would be lower.

## *5.10 Process Yields*

An important feature of the process, which enables the comparison of it with other processes, is the concept of process yields. The process yields are given in table 5.6.
The streams entering the battery limit are the feed (wood chips), the make-up streams (water and methanol), cooling water and boiler feed water. The streams leaving the battery limit are the product (pulp), biogas, biomass, wastewater and cooling water. This information can be deduced from figure 2.1 (chapter 2). Because there are no other plants using the same kind of process, there is no reference for these process yields. It does become clear from table 5.6 that the process uses a lot of cooling water (CW).
When the totals of IN and OUT streams are compared, a difference can be noticed. This arises from the fact that lignin and part of the biogas are burnt in the furnace. In the furnace these streams are converted to flue gasses and ash. The magnitudes of these streams are unknown, but the sum of them should be the difference between the total of the streams going into the plant and those going out, i.e. (53.2 +6) – 47.4 = 11.8 t/h.

Table 5.6: Process yields.

| Process Streams | | | | | | | |
|---|---|---|---|---|---|---|---|
| Name | Ref. Stream | kg/s | | t/h | | t/t pulp | |
| | | IN | OUT | IN | OUT | IN | OUT |
| Feed | <01> | 14.58 | | 52.5 | 0.0 | 3.64 | 0.00 |
| **Pulp Product** | <32> | | 4.04 | 0.0 | 14.4 | 0.00 | **1.00** |
| Biogas Product | <27> | | 0.87 | 0.0 | 3.1 | 0.00 | 0.22 |
| Make-up methanol | <17> | 0.12 | | 0.4 | 0.0 | 0.03 | 0.00 |
| Make-up water | <40> | 0.07 | | 0.3 | 0.0 | 0.02 | 0.00 |
| Biomass | <29> | | 0.81 | 0.0 | 2.9 | 0.00 | 0.20 |
| Shives | <12> | | 0.08 | 0.0 | 0.3 | 0.00 | 0.02 |
| Wastewater | <38> | | 7.39 | 0.0 | 26.6 | 0.00 | 1.84 |
| Total | | 14.77 | 13.18 | 53.2 | 47.4 | 3.69 | 3.28 |

| Utilities | | | | | | | |
|---|---|---|---|---|---|---|---|
| Name | Ref. Stream | kg/s | kW | t/h | kWh/h | t/t pulp | kWh/ t pulp |
| BFW | - | 1.783 | | 6 | | 0.44 | |
| CW | - | 581.35 | | 2093 | | 145.08 | |

# 6 Process Control

In a chemical plant it is important to continuously monitor process variables and to take appropriate control action, whenever deviations of the process variables of their desired values occur. Process variables are controlled through manipulated variables. Manipulated variables are variables, which can be adjusted freely.

The primary objectives of process control are:

- Safe plant operation, the process variables should be kept within known safe operating limits to prevent the development of dangerous situations
- Production rate, to achieve the desired product output
- Product quality, it is important to maintain the product composition within the specified quality requirements
- Cost, it is important to operate at the lowest production cost

Instruments are provided to monitor the key process variables during plant operation. The process variables are measured with sensors. The most commonly used sensors are flow sensors, pressure sensors, temperature sensors and composition analyzers. The sensor transmits a signal to a controller. The controller compares the sensor signal with the set point value, the desired value of the process variable. When a deviation of the set point value is determined, a control signal is sent to the final control element. Control elements receive the output of the controller and adjust accordingly the value of the manipulated variable.

In the plant four types of controllers and two types of control systems are used: ratio control and override control.

The following types of controllers are used:

- Temperature controller (TC), adjusts the temperature of a certain flow or unit
- Pressure controller (PC), adjusts the pressure of a certain flow or unit
- Flow controller (FC), adjusts the flow rate of a certain flow.
- Level controller (LC), adjusts the interface between two phases in a certain unit

Ratio control (ref. 25) is a special type of control system where two disturbances are measured and held in a constant ratio to each other. Both flow rates are measured but only one can be controlled. The stream whose flow rate can freely be chosen is referred to as wild stream. The ratio control can be performed in two ways:

- Both flow rates are measured and their ratio is taken. This ratio is compared to the desired ratio and the deviation between the measured and desired ratios constitutes the actuating signal for the ratio controller
- The flow rate of the wild stream is measured and multiplied by the desired ratio. The result is the flow rate that the other stream should have and constitutes the set point value, which is compared to the measured flow rate of the stream. The deviation constitutes the actuating signal for the controller, which adjusts appropriately the flow of this stream.

In the plant ratio control is performed according to the first alternative

Override control (ref. 25) is used for the protection of process equipment. During the normal operation of a plant or during its start-up or shutdown it is possible that dangerous situations may arise which may lead to destruction of equipment and operating personnel. In such cases it is necessary to change from the normal control action and prevent a process variable from exceeding an allowable upper or lower limit. The high selector switch (HSS) is used whenever a variable should not exceed an upper limit, and the low selector switch is employed to prevent a process variable from exceeding a lower limit.

In the following sections the process control applied in the plant is explained.

## *6.1 Steam Explosion*

The steam explosion section consists of three sections: a presteaming section, a high pressure heating section and an explosion section. All three sections are equipped with process controls.

### 6.1.1 Presteaming section (X02)

In the presteaming section it is important that the temperature of the wood chips is raised from 10°C to 80°C. A temperature controller is installed that measures the temperature in this section and takes control action whenever a deviation of the set point is detected. The set point is set on 80°C. If a deviation of this set point is detected, a control signal is transferred from the temperature controller to the valve in the low-pressure steam pipeline. The opening of the valve is altered in such a way to smooth out the deviation.

### 6.1.2 High pressure heating section (X03)

The temperature of the wood chips in the high pressure heating section must be raised from 80°C to 190°C. The temperature is raised due to the supply of high-pressure steam. The temperature in this section is controlled with a temperature controller. This controller changes the set point of the flow controller, which controls the flow-rate of high-pressure steam from the boiler to the high-pressure steam section. If the temperature in the high-pressure heating section has dropped below 190°C, a deviation of the set point (190°C) is detected by the temperature controller. The controller increases the set point of the flow controller, which subsequently increases the flow rate of high-pressure steam.

### 6.1.3 Steam explosion section (V01)

The important control variable in the steam explosion section is the pressure at which the wood chips are discharged. The pressure is generated with a screw press, which presses the wood chips together and in this way the pressure is increased. A low pressure will lead to an inefficient performance of the steam explosion (wood chips are too big), whereas high pressures can lead to dangerous situations (ruptures in the steam explosion vessel or discharge lines). The set point is set on 12.6 bara. A pressure controller detects deviations of this set point and consequently adjusts the set point of the speed controller of the screw.

Because of the high pressures that are generated in the screw the section should be equipped with alarm system. These systems should alert the operators for the potentially dangerous situation when the pressure in the screw has increased above the maximum allowable pressure. The operators can then take appropriate action.

### *6.2 Extractor (R01)*

There should be a constant ratio between the amount of wood (stream 9) that enters the extractor and the flow rate of the solvent (stream 13) to the reactor. This ratio is important to keep the extractor at its optimum operating conditions and to make sure the lignin requirements of the final pulp are satisfied. The wood supply to the extractor is considered the wild stream. When the wood supply increases, the ratio wood to solvent decreases. This decreased ratio is compared with the desired ratio (set point) and a deviation is measured. The solvent flow rate should be increased to maintain the optimum wood to solvent ratio in the extractor. Therefore the valve in the solvent pipeline is opened in such a way that the desired ratio is reached again. The opposite is true when the wood supply to the extractor decreases.

However the ratio control can be overridden when the liquid level in the mixer (M01) has risen to the maximum safe level. Above this level danger of flooding of the mixer exists. The override control transfers a signal to the flow controller of the solvent stream to increase the flow rate of solvent. The high selector switch receives two signals: one from the ratio controller and one from the override controller. The high selector switch sends the signal with the highest value (in this case the signal from the override controller) to the flow controller of the solvent stream and the valve is opened and the level in the mixer decreases. The wood to solvent ratio temporarily deviates from the desired ratio.

The level in the extractor is controlled by speed control of the motor, which regulates the speed of the conveyor belt. When the level increases above the set point, the level controller transfers a control action to the speed controller of the conveyor belt. The set point of the speed controller is altered. The speed of the conveyor belt and consequently the amount of pulp discharged is increased.

Another important control variable in the extractor is the pressure. If the pressure in the extractor is too low, methanol vapors are formed. The temperature in the extractor is 190°C and the vapor pressure of methanol at this temperature is 33 bara. When the pressure in the extractor drops below this vapor pressure, methanol vapors are formed. These vapors can leave the extractor and this will lead to dangerous situations. Methanol is poisonous for the workers and also flammable (risk of fire and explosion).
Also an increase in pressure is dangerous. The chance of ruptures in the extractor or discharge lines increases with increasing pressure. The pressure in the extractor is controlled with the flow controller on the valve after the solvent pump in stream 13. If the pressure in the extractor increases above the set point of 33 bara, the valve is opened and the pressure on the solvent stream is released. The solvent is brought to a lower pressure level and consequently the pressure in the extractor drops. The opposite is true if the pressure in the extractor decreases.

For safety reasons an alarm system and a pressure relief valve are placed on the extractor. The alarm system should alert the operators when the temperature or pressure in the extractor vessel has reached its maximum allowable value. However delay or lack of response by the operator is likely to lead to a rapid development of a dangerous situation (possible explosion of the extractor) and therefore also a pressure relief valve is installed. The pressure relief valve is activated when the pressure in the extractor has reached a pressure of 36 bara, the maximum pressure that the reactor is able to safely withstand. When the relief valve is activated, the contents of the reactor are discharged in a dump vessel.

Finally the temperature in the extractor is controlled. The set point is set at 190°C. The temperature should be measured for safety and kinetic reasons. The temperature in the extractor is controlled with the temperature of the ingoing solvent stream. The temperature of the solvent stream is controlled with the amount of steam that is led through the heat exchanger (E03). The reactions that take place in the extractor are moderate exothermic. The appearance of hot spots is not expected to take place. Therefore the temperature is only measured with one thermocouple halfway down the reactor vessel and not with several thermocouples placed on several points in the extractor. The temperature controller controls the flow of high-pressure steam through the heat exchanger.

At the end of the process pulp is submitted to a quality control. Samples are taken from the pulp and the lignin content, the moisture content and the viscosity of the pulp are measured. Whenever the lignin content of the pulp is too high, appropriate control action is taken. The solvent to wood ratio can be increased by adapting the set point of the ratio controller. Also the temperature in the extractor and consequently the pressure in the extractor can be increased. However an increase in temperature is detrimental for the average chain length of the cellulose molecules. Also the residence times in the extractor can be increased by decreasing the set point of the speed controller on the conveyor belt.
The viscosity of the pulp is a measure for the average chain length of the cellulose polymers. A shorter chain length decreases the quality of the pulp. So when the viscosity of the pulp is too low, and thus the average chain length of the cellulose polymers is to short, also appropriate control action is taken, the temperature in the extractor is decreased. So the set point for the temperature controller is decreased and consequently the set point for the pressure controller is decreased. The vapor pressure of methanol decreases when the temperature is decreased. Also the set point of the speed controller on the conveyor belt can be increased. An increase in the speed of the conveyor belt decreases the residence times in the reactor.

### *6.3 Distillation column (C01)*

The temperature in the distillation column is controlled by the discharge of the compressor (K01). If the compressor discharges more methanol vapor, more methanol condenses in the heat exchanger (E09) and more heat can be transferred in the heat exchanger. As a result the temperature of the bottom stream of the distillation column is increased. The discharge of the compressor is controlled by the speed of the motor. When the temperature in the column decreases below the set point of the temperature controller, a deviation is measured. A control signal is transferred to the speed controller of the motor to increase the discharge of methanol. However to prevent the

discharge pressure of the compressor from exceeding an upper limit, an override control with a high switch selector (HSS) is introduced. It transfers control action from the temperature control to the pressure control loop whenever the discharge pressure exceeds the upper limit. A higher discharge pressure will lead to condensation of methanol and this will lead to a strong decrease in heat transfer across the surface of the heat exchanger.

The pressure in the column is controlled by the amount of vapor that is withdrawn from the top of the column. The pressure controller sets the set point of the flow controller that regulates the flow rate of vapor out of the column, by altering the opening of the valve. If the pressure in the column is too high, the flow rate of vapor out of the column should be increased.

The temperature in the top of the column is an indication for the composition of the distillate. Methanol is the lower boiling component (boiling point of 65°C), whereas water is the higher boiling component (100°C). If the temperature in the top of the column increases, this is an indication that the water content in the distillate increases. A better separation has to take place to decrease the water content, because else too much water is sent back to the process. A better separation can be accomplished by increasing the reflux ratio that is by increasing the amount of liquid that is sent back to the column. Therefore the temperature controller in the top of the column sets the set point of the flow controller on the pipeline from the buffer vessel (V05).

The liquid level in the bottom of the distillation column is controlled by the liquid level in the liquid/vapor splitter (communicating vessels) (V06). The liquid/vapor splitter is equipped with a level controller. If the liquid level in the distillation column increases, the liquid level in the liquid/vapor splitter also increases. The level controller detects a deviation from the set point and transfers a control signal to the valve. The valve is opened and the flow to the fermentor is temporarily increased, until the level in the liquid/vapor splitter has reached its set point value again.

The vapor from the top of the column is pressurized with a compressor and subsequently passed through a heat exchanger where heat exchange takes place with the bottom flow of the distillation column. The condensation of the top flow vapor takes place under pressure and therefore the condensed liquid is also pressurized. In the pipeline to the buffer vessel (stream 25) a pressure relief valve is installed. A pressure controller is installed on this valve to control the pressure of the stream to the buffer vessel, which operates at 1 bar.

### *6.4 Dryers ((D01 and D02)*

The pulp and the lignin that exit the dryers should satisfy certain quality requirements. The pulp should not contain more than 6 v% moisture to satisfy the customers' requirements. The lignin may also not contain too much moisture. The heat of combustion of lignin decreases when the moisture content increases. It is therefore important to measure the moisture content of the pulp and the lignin after the dryers and to take appropriate control action when the moisture content is too high or too low.
The moisture content of the pulp and the lignin is measured with a hygrometer. A hygrometer is an instrument that measures the moisture content of air. The moisture

content in the air at the end of the dryer is related to the moisture content in the pulp or the lignin that exits the dryer (the moisture in the air is in equilibrium with the moisture in the lignin or pulp).

Control action is taken when the moisture content of the pulp or the lignin is too low or too high. If the moisture content is too high, the low-pressure steam supply must be increased. The valve that controls the steam flow is opened to increase the steam flow through the tubes in the dryer. This increase in low-pressure steam, will lead to an increased heat supply to the dryer. As a result of this increase in heat more methanol and water will evaporate and the moisture content in the pulp or lignin will decrease.

### *6.5 Mixers*

#### 6.5.1 Solvent Feed Mixer (M01)

The composition of methanol and water in the mixture must remain at a constant value of 75 w% methanol and 25 w% water. This is the optimum composition for the extraction of lignin from the wood chips. If a deviation of this composition is detected, methanol and water must be supplied in such a way that the required composition is reached again.
The composition of the mixture is determined with the index of refraction. The index of refraction can be related to the amount of methanol and water in the mixture. In this way appropriate control action can be taken whenever deviations are observed.
When a deviation of the set point is detected, the flow rates of methanol and water make up are altered to bring the composition in the mixer vessel back to the set point.

The level in the mixture is controlled with an override controller. If the level increases above a certain set point a control signal is sent to the high selector switch, which consequently adapts the flow of solvent to the extractor (see extractor).

#### 6.5.2 C01 Feed Mixer (M02)

The liquid level in the mixture is the important control variable. The level in the mixer should remain within certain bounds to prevent flooding or emptying. The level is controlled with a level controller, which passes a signal to the flow controller in the discharge pipeline (stream 33). The level controller adapts the set point of the flow controller, whenever level control is required. In this way flooding or emptying of the mixer is prevented.

### *6.6 Flash vessels ((V02 and V03)*

In the flash vessels the liquid is flashed from a high pressure to a lower pressure (the pressure in the drum). Vapor is produced and reaches equilibrium with the remaining liquid. The flashes that are executed are adiabatic flashes. Therefore heat is not added to the flash vessels and temperature control is not necessary. The important control variable during the flash is the pressure in the vessel. The pressure in the flash vessel should be dropped to 1 bar to make sure that the maximum amount of liquid flashes. A larger pressure drop means a vapor liquid equilibrium with more vapors. The pressure controller is coupled to a valve controlling the flow of vapor out of the flash

vessel. It is also important to control the liquid levels in the flash vessels. The level of the vapor liquid interface may change. However the liquid level should remain within certain bounds. Therefore a level controller is installed that adjusts the level in the vessel by manipulating the flow of liquid out of the drum.
Finally a pressure relief valve is placed on the vessels for safety reasons. The relief valve is activated when the pressure in the flash vessel has reached the relief set pressure. The relief set pressure is set on 5 bara, the maximum pressure that the vessel is able to safely withstand. The vapor released from the relief valve is then collected in a dump vessel.

### *6.7 Screw Press (X05)*

The important control variable of the screw press is the pressure in the screw. The pressure at the end of the press may not rise above a certain pressure level, because this can cause damage to the press. Moreover the pressure may also not be too low. Low pressure will lead to an inefficient removal of the solvent from the pulp. Too much solvent remains in the pulp and the pulp requirements are not satisfied. Furthermore low pressure will lead to the formation of methanol vapors. The pressure in the screw press is controlled with the speed controller of the motor. When the pressure is too low the speed of the motor is increased. The set point is set on 33 bara.

### *6.8 Fermentors (V04)*

Flow controllers are installed to control the discharge of biogas, wastewater and biomass out of the fermentor. The wastewater stream is split into two parts. One part is cooled and sent back to the reactor, whereas the other part is discharged. The amount of wastewater that is sent back to the reactor is determined by the flow controller. The level controller of the fermentor determines the set point of the flow controller.

An important control variable in the fermentor is the temperature. The fermentor should be maintained at 40°C, the optimum temperature for the growth of the bacteria. Therefore a temperature controller is installed. This controller regulates the temperature in the fermentor with the temperature of the ingoing stream. The temperature of the ingoing stream can be controlled by altering the flow of cool water through the heat exchanger.

Furthermore the pH of the liquid in the fermentor must be regulated. The pH at which the growth rate of the bacteria is optimum is 7.7. Therefore the set point for the pH controller is a pH of 7.7. The pH is controlled through the supply of a caustic solution (stream 41). The pH controller sets the set point of the flow controller on the caustic solution supply. In this way an optimal growth environment for the bacteria is created.

### *6.9 Heat exchangers (E01 to E11)*

At different places in the process heat exchangers are installed to heat or cool certain streams. These heat exchangers are equipped with temperature controllers, which control the amount of steam or cooling water that flows through the heat exchangers. When a deviation of the set point is detected, control action is taken. The flow of

steam or cooling water through the heat exchanger is increased or decreased with a valve installed on these streams.

Especially at places where vapors are condensed and subsequently led through pumps, it is important that full condensation of the vapors and cooling of the liquids has taken place. When the vapors are not fully condensed or the temperature of the liquid is too high, cavitation can occur in the pumps. Cavitation occurs when bubbles of vapor are present or formed in the pump casing. Vapor bubbles will form if the temperature of the liquid is above the saturated temperature of the mixture at the inlet pressure of the pump. This can cause damage to the pumps. It is therefore important that full condensation and cooling has taken place in the heat exchangers.

### *6.10 Buffer tanks (V05, V06, M01 and M02)*

The only important process variable for the buffer tanks is the liquid level. The level should be retained within certain levels. Therefore liquid controllers are installed, that control the level by altering the opening of the valves on the outgoing streams.

### *6.11 Valves*

At different places in the process valves are installed to control the flow rate of the stream leaving the valve. The most common used valve is the pneumatic valve. This is an air-operated valve that controls the flow through an orifice by positioning appropriately a plug. The flow through the valve is determined by the pressure drop across the valve. In a process different pretreatment, conversion and separation steps take place that all work at a certain pressure. These pressures should be maintained at their desired values, because differences in pressure can lead to unsafe situations, but also to incorrect performance of the conversion and separation steps. Flow controller are therefore installed on the valves. The pressure of the flow after the valve is measured and compared with the desired value. Appropriate control action is taken (valve opening increased or decreased) whenever deviations are measured.

### *6.11 Pumps (P01 to P10)*

The pumps in the process all work at a certain capacity. A liquid flow or slurry of certain flow rate is brought at a certain pressure. The flow that leaves the pump is controlled with a flow controller, which controls the positioning of the plug in the valve.

# 7 Mass and Heat Balances

This chapter demonstrates the mass and heat balances of the total process and of all pieces of equipment.

## *7.1 Mass and heat balance for the total plant*

The streams entering and leaving the plant are summarized in table 7.1. In this summary the lignin and the LP steam are taken as outgoing flow, whereas the HP steam is taken as entering flow, because we don't take the furnace and the cooling tower into account. It was beyond the scope of the project to determine the mass and heat contents all flue gases and ashes from the furnace. In appendix 7.2 the calculations of the enthalpy balance are explained in more detail.

Table 7.1: In and outgoing streams of the plant

| *Stream name* | *Stream number* | *Entering stream* | | *Outgoing streams* | |
|---|---|---|---|---|---|
| | | Mass (kg/s) | Heat (kW) | Mass (kg/s) | Heat (kW) |
| Feed | <1> | 14.583 | -139304 | | |
| HP steam | <2> | 2.508 | -32950 | | |
| Make-up methanol | <17> | 0.118 | -888 | | |
| Make-up water | <40> | 0.072 | -1149 | | |
| LP steam | <7> | | | 0.725 | -9593 |
| Shives | <12> | | | 0.083 | -568 |
| Lignin | <24> | | | 1.776 | -9765 |
| Biogas | <27> | | | 2.433 | -19060 |
| Biomass | <29> | | | 0.810 | -4978 |
| Pulp | <32> | | | 4.035 | -20485 |
| Waste water | <38> | | | 7.420 | -116805 |
| **Total** | | **17.281** | **-174292** | **17.281** | **-181253** |

The mass balance is closed, as can been seen from the table above. The heat balance can be completed when all heaters, coolers, dryers, condensers and pumps are considered. The difference in the enthalpy for all the streams is (-181253) – (-174292) = -6961 kW. So this enthalpy is withdrawn. This will be validated in paragraph 7.2.

## *7.2 Mass and heat balance for each piece of equipment*

For every unit the mass and heat balance is made. These are tabulated in appendix 7.1. Afterwards all the balances were checked. Again the mass balances are closed and the deviation in the energy balance is only 3 kW and this is caused by round-off errors. Therefore the energy balance is closed too.

## *7.3 Mass and heat balance for stream components*

For every component a mass balance is made over the whole plant. The sum of the changes in mass per component should add up to zero. The overall mass balances for each component can be found in table 7.2.

Table 7.2: Overall mass balances

| *Overall Component Mass Balance & Stream Heat balance* | | | | | | | |
|---|---|---|---|---|---|---|---|
| STREAM Nr. : | | 1+2+17+40 | IN | 7+12+24+27+29+32+38 | OUT | | OUT-IN |
| Name : | | Total Plant | | Total plant | | Total plant | |
| COMP | MW | kg/s | kmol/s | kg/s | kmol/s | kg/s | kmol/s |
| Cellulose | 150000.00 | 3.94 | 0.0000 | 3.51 | 0.0000 | -0.43 | 0.0000 |
| Hemicellulose | 1000.00 | 2.08 | 0.0021 | 0.28 | 0.0003 | -1.80 | -0.0018 |
| Lignin | 3000.00 | 1.84 | 0.0006 | 1.68 | 0.0006 | -0.16 | -0.0001 |
| Extractives | 519.00 | 0.24 | 0.0005 | 0.03 | 0.0001 | -0.21 | -0.0004 |
| Minerals | 100.00 | 0.13 | 0.0013 | 0.05 | 0.0005 | -0.08 | -0.0008 |
| Water | 18.00 | 8.92 | 0.4958 | 8.78 | 0.4880 | -0.14 | -0.0077 |
| Methanol | 32.00 | 0.12 | 0.0037 | 0.08 | 0.0026 | -0.03 | -0.0011 |
| Acetic acid | 60.00 | 0.00 | 0.0000 | 0.02 | 0.0003 | 0.02 | 0.0003 |
| Biomass | 26.17 | 0.00 | 0.0000 | 0.40 | 0.0154 | 0.40 | 0.0154 |
| Methane | 16.00 | 0.00 | 0.0000 | 0.64 | 0.0400 | 0.64 | 0.0400 |
| Carbon dioxide | 44.00 | 0.00 | 0.0000 | 1.79 | 0.0408 | 1.79 | 0.0408 |
| Monosaccharides | 150.00 | 0.00 | 0.0000 | 0.00 | 0.0000 | 0.00 | 0.0000 |
| Total | | 17.28 | 0.5040 | 17.28 | 0.5886 | 0.00 | 0.0847 |
| Press. | Bara | | | | | | |
| Temp | ºC | | | | | | |
| Enthalpy | kW | -174292 | | -181253 | | -6961 | |

As can be seen in table 7.2 the mass balance is consistent. Also from this analysis follows that the total extracted heat during the process contains –6961 kW, which is consistent with paragraph 7.1 and 7.2.

# 8 Process and equipment design

## *8.1 Process simulation*

The following problems were encountered with flow sheet programs like Aspen:

- Willow wood mainly consists of macromolecules. Components like cellulose and lignin aren't available in the database of such a program.
- Wood chips are solid particles with a complex composition and structure. The different components of the wood chips are chemically bound to each other and this can't be imported in Aspen.
- Processes like steam explosion aren't very basic unit operations and are therefore difficult to simulate in flow sheet programs.

Several attempts were made to simulate the whole process in Aspen. An input file for the components of wood was found (ref. 140). The components in this file were only partly defined and could not be used for a reliable simulation. For the last two problems we couldn't find a way to make the Aspen simulation work. Therefore only a part of the process is simulated in Aspen. A flow sheet of this simulation can be found in appendix 8.17.

The recovery of the solvent is completely simulated in Aspen$^+$ version 11.1. In the Aspen simulation methanol and water are the only components that were taken into account. The results from Aspen are combined with Excel (used version MS Excel 2000) calculations. In Excel the mass balances and enthalpy balances are calculated for all the components. Aspen is especially used for the calculations in which vapor-liquid equilibriums played an important role like flash calculations. This way of interaction between the two programs was the best way to make a reliable simulation in the time given for the CPD project. Next an example of this interaction will be given.

Stream 15 contains 50 w% solvent and 50 w% pulp. The temperature of this stream is 190 °C and the pressure is 33 bara. Subsequently the pressure is released in a flash vessel to 1 bara. A part of the solvent is flashed off. We assumed that the other components present in the stream don't influence the vapor liquid equilibrium of water and methanol. In Aspen the flashing of the solvent stream is simulated. The temperature during the flash drops to 74 °C. Methanol and water cool down to 74 °C, but also the pulp. The temperature decrease of the pulp delivers energy for the evaporation of solvent and therefore this amount of energy is calculated in Excel. Next the Aspen simulation is done again and now the energy from the cooling of the pulp is used as heat duty for the flash. The amount of flashed solvent is now known and the mass balances can be finished in Excel. Another assumption made is that the only components that are able to flash are water and methanol. So species like cellulose remain completely in the liquid phase.

Another, not Aspen-related problem was the presence of the substance hemicellulose. Hemicellulose is hydrolyzed in the process and is therefore partly split up into monosaccharides and acetic acid. Because hemicellulose contains several types of monosaccharides, some C5, some C6, it is almost impossible to model this. Because it is plausible that these monosaccharides react in almost the same way as the hemicellulose itself and are quite harmless in our process, they are lumped into one

group, still called monosaccharides. The only component that is more reactive is the acetic acid. Therefore this is taken into account from the reactor onwards, because after the reactor most of the acetic acid is present.

## *8.2 Equipment selection and design*

### 8.2.1 Steam explosion equipment

The wood chips are pretreated with low-pressure steam (1-2 bar) to achieve a uniform humidity. Subsequently the chips are brought into contact with high-pressure steam (12.6 bar, 190 °C). After a residence time of several minutes a pressure valve opens and the steam explosion will take place. This causes some of the condensed steam to evaporate. Part of this steam is used to pretreat the wood chips. The severity of the steam explosion ($R_0$) can be calculated with:

$$R_0 = t \cdot \exp\left[\frac{T-100}{14.75}\right] \qquad (8.1)$$

with: t = contact time with high pressure steam in minutes
T = temperature of high pressure steam in °C

In literature it is common to express the severity in logarithmic form (log $R_0$). A higher severity decreases the chain length of the cellulose. And a lower severity leads to more fragmentation of the wood chips. From the article by Joseffson (ref. 66) we have chosen a log ($R_0$) of 3.5. The contact time necessary follows from mass transfer considerations (see appendix 8.2). The temperature follows from the severity and the contact time and turns out to be 190 °C. The saturated pressure of steam at this temperature is 12.6 bar. At these conditions the dimensions of the wood chips are reduced from 30x30x10 mm to 5x5x2 mm (San Martin, ref.68).

In the following drawing the steam explosion system of the company Stake Technology Ltd. is shown.

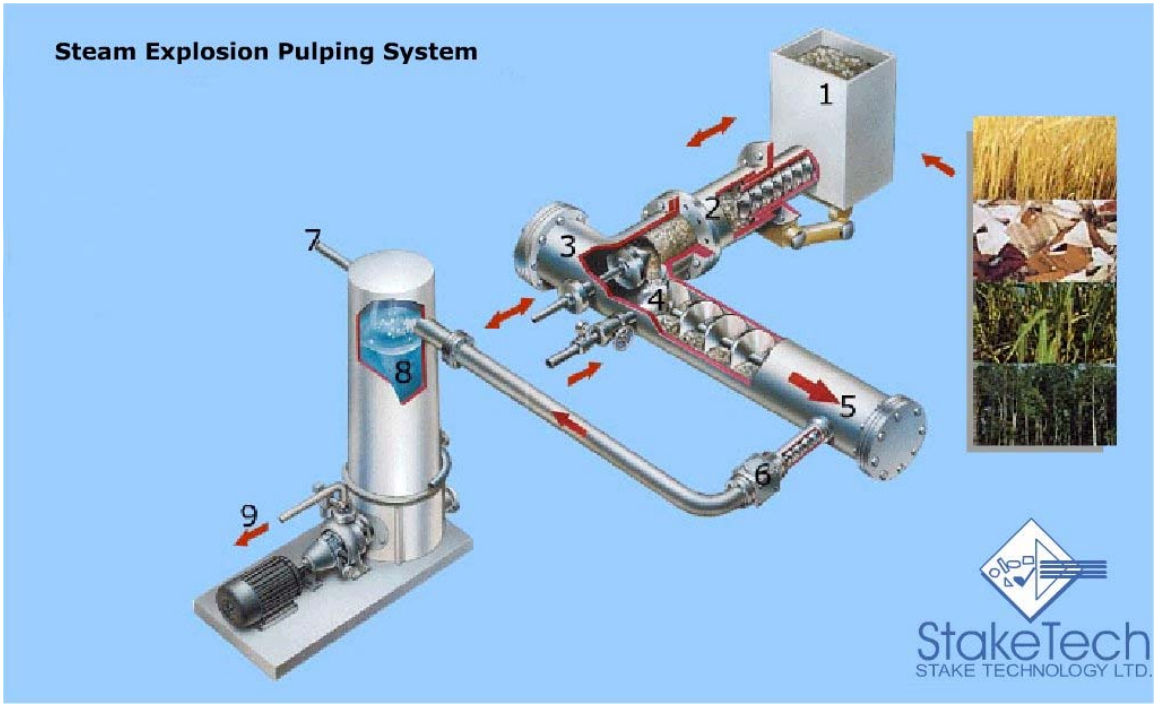

Figure 8.1: Steam explosion system

In our process the amount of wood chips that enter the steam explosion equipment is 420 kton/a. These wood chips contain 43.5% water. Therefore the amount of dry wood chips entering the steam explosion equipment is 237.3 kton/a. This is equal to $237.3 \cdot \frac{1000}{8000} = 29.7$ dry ton/hr.

The maximum capacity of one steam explosion apparatus is 15 dry ton/h. The specification of this piece of equipment can be found in table 8.1.

Table 8.1: Dimensions and design variables of the steam explosion

| *Equipment dimensions and parameters* | |
|---|---|
| Capacity (dry ton/h) | 15 |
| Width, length, height of feeder (m) | 4.9 x 1.8 x 7.6 |
| Width, length, height of digester (m) | 8.1 x 5.9 x 16.0 |
| Weight of feeder (ton) | 55 |
| Weight of digester (ton) | 110 |
| Energy consumption (kWh/dry ton) | 16.8 |
| Total energy consumption (kW) | 250 |
| Contact time (min) | 7.0 |
| Temperature before explosion (°C) | 190 |
| Temperature after explosion (°C) | 115 |
| Pressure before explosion (bara) | 12.6 |
| Pressure after explosion (bara) | 1.7 |
| High pressure steam consumption (ton/h) | 4.5 |
| Low pressure steam production (ton/h) | 3.5 |
| Purchased equipment cost (€) | 3,000,000 |
| Material of construction | Stainless steel |

Two of these steam explosion installations will work in parallel. At the temperature of 190 °C the hemicellulose is partly hydrolyzed. Therefore acetic acid is formed. As material of construction stainless steel is used.

8.2.2 Pressure screen (S01)

The different types of screeners were discussed in chapter 5 and appendix 5.3. We selected a pressure screen as the best screening device. Figure 8.2 shows a schematic drawing of a pressure screen.

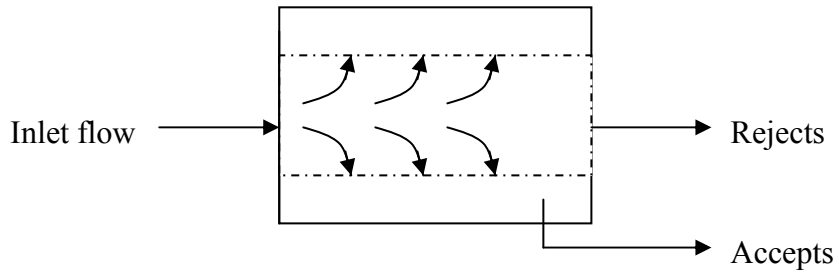


Figure 8.2: Pressure screener

The dimensions of the wood chips after the steam explosion are 5x5x2 mm. Therefore they can easily pass the holes of 8 mm in the pressure screen. The area required can be calculated with the method of Matthews (ref. 22):

$$A = \frac{0.4 \cdot C_t}{C_u \cdot F_\infty \cdot F_s} \qquad (8.2)$$

with:
- $A$ = Screen area [$m^2$]
- $C_t$ = Throughput rate [kg/s]
- $C_u$ = Unit capacity [$kg/s/m^2$]
- $F_\infty$ = Open-area factor [-]
- $F_s$ = Slotted-area factor [-]

$C_u$ depends on the handled material. $C_u$ isn't found in literature for pulp and therefore the value for coke is used to perform the calculations. $F_\infty$ depends on the sizes and the spacing between the holes in the screen. $F_s$ depends on the geometry of the holes.
The rejects contents of the feed is estimated to be 2.5 w% of the solids present in the feed (ref 1). The screening efficiency of the pressure screen is calculated in appendix 5.3 and turns out to be 80% and therefore $0.80 \cdot 2.5 = 2.0$ w% of the solids present in the feed stream is rejected.

Table 8.2: Dimensions and design variables of the pressure screen (S01)

| *Equipment dimensions and parameters* | |
|---|---|
| Capacity (kg/s) | 16.62 |
| Holes (mm) | Squares of 8 x 8 mm |
| Area of screen ($m^2$) | 9.78 |
| Type of plate | Cylindrical, Aperture type |
| Length (m) | 3.06 |
| Diameter (m) | 1.02 |
| Pressure drop (bara) | 0.70 |
| Temperature (°C) | 115 |
| Energy consumption (kWh/t) | 20 |
| Total energy consumption (MW) | 1.18 |
| Screening efficiency | 0.80 |
| Purchased equipment cost (€) | 32,000 |
| Material of construction | Stainless steel |

8.2.3 Extractor (R01)

The extractor operates continuously (see appendix 2.1). Solvent and pulp are contacted cocurrently. To calculate the volume of the extractor the assumption is made that the extractor behaves as a plug flow reactor. This is because a conveyor belt transports the mixture of solvent and pulp. The extractor doesn't have many similarities with the continuously operating Kamyr digesters (see appendix1.2) commonly used in the Kraft processes, but looks much like the M&D digester. This digester used is often used to pulp sawdust. After the steam explosion the wood chips are very alike sawdust.

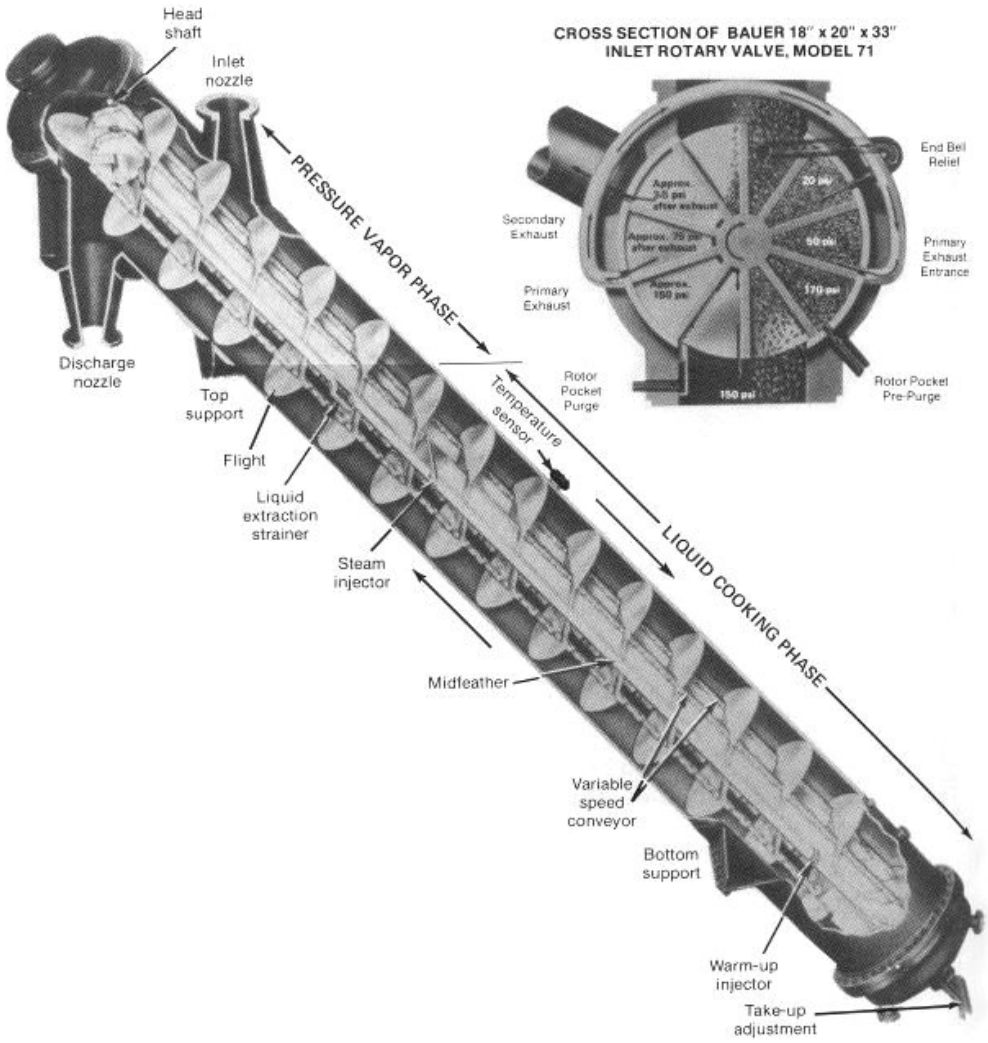


Figure 8.3: M&D digester

The operating pressure of the extractor is 33 bara. At this pressure the solvent is still liquid at the extraction temperature of 190 ºC. At these pressures a special feeder is needed (see appendix 8.4 and figure 8.3).

From the assumed first order kinetics for the delignification rate of lignin and the assumed plug flow the volume of the extractor is 205.5 $m^3$. The length to diameter ratio is 10:1. The maximum diameter of an M&D digester is 3.0 m.

Table 8.3: Dimensions and design variables of the extractor (R01)

| *Equipment dimensions and parameters* | |
|---|---|
| Capacity (kg/s) | |
| Liquor to wood ratio | |
| Volume ($m^3$) | 205.5 |
| Length (m) | 29.7 |
| Diameter (m) | 2.97 |
| Weight (ton) | 145 |
| Residence time (h) | 0.64 |
| Pressure (bara) | 33.0 |
| Temperature (°C) | 190 |
| Energy consumption feeder (kW) | 101.6 |
| Energy consumption conveyor belt (kW) | 353.0 |
| Cellulose yield (%) | 87.2 |
| Purchased equipment cost (€) | 2,500,000 |
| Material of construction | Stainless steel |

### 8.2.4 Screw press (X05)

The screw press is a mechanical device, which is used for liquid/solid separation. With a screw press it is possible to compress the pulp to a cake and at the same time to dewater the pulp by squeezing it. This process is only suitable for the dewatering of rough organic materials, pastes, sludges or similar materials.

The screw press delivers pulp with a consistency of 50 w%. The selected screw press is from the firm FKC Screw Press and the type is SHX-1200x8000L.

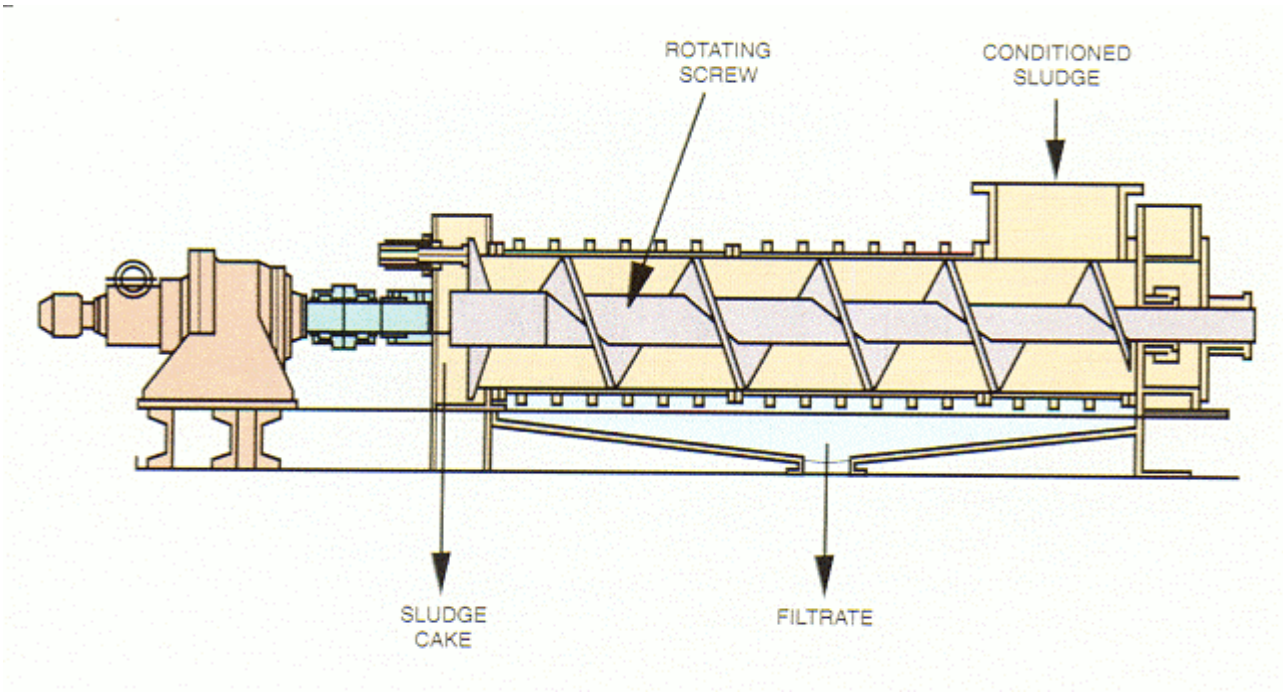


Figure 8.4: Screw Press

From the consistency the mass balances can easily be calculated (see appendix 8.5).

Table 8.4: Dimensions and design variables of the screw press (X05)

| *Equipment dimensions and parameters* | |
|---|---|
| Ingoing solid content (w%) | 9 |
| Outgoing solid content (w%) | 50 |
| Capacity (dry ton/h) | 300 |
| Diameter (m) | 1.20 |
| Length (m) | 8.00 |
| Pressure (bara) | 33 |
| Temperature (°C) | 190 |
| Energy consumption (kW) | 186 |
| Price (€) | 500,000 |

### 8.2.5 Flash vessels and vapor/liquid splitter at the column

After the screw press most of the solvent is separated from the pulp. Both streams leaving the screw press have a pressure of 33 bara and 190 °C. Therefore a part of the solvent from both streams can easily be flashed of. At stream <15> (V02) the solvent has to be removed from the product and at stream <18> (V03) the solvent has to be removed from the dissolved lignin and hemicellulose. In both cases the solvent is condensed afterwards and recycled to the extractor.
The phase splitter (V06) is sized with the same equations as the flash vessels and is therefore described in this paragraph.
The dimensioning calculations of these three pieces of equipment can be found in appendix 8.6.

Table 8.5: Dimensions and design variables of the flash vessels

| | *Flash (V02)* | *Flash (V03)* | *Phase splitter (V06)* |
|---|---|---|---|
| Length (m) | 3.48 | 12.8 | 8.35 |
| Diameter (m) | 1.16 | 2.54 | 2.09 |
| Feed flow rate (kg/s) | 7.38 | 46.1 | 24.5 |
| Pressure of feed (bara) | 33 | 33 | 1 |
| Flash pressure (bara) | 1 | 1 | - |
| Feed temperature (°C) | 190 | 190 | 98.1 |
| Flash temperature (°C) | 74.1 | 72.9 | - |
| Vapor/liquid ratio | 1.69 | 0.94 | 1.65 |
| Purchased cost (€) | 20,100 | 133,200 | 34,900 |

### 8.2.6 Hydrocyclone (S02)

The cyclone is used to separate the precipitated lignin quickly from the solvent. For the sizing the dimensionless model is used. The most important design variable is the cut size $x_{50}$. The cut size is the particle diameter at which the separation efficiency is 50 %. Larger particles are mainly separated to the underflow and smaller particles to the overflow. The particle size distribution of lignin is unknown and therefore a very low cut size is chosen. In this way the lignin particles are large compared to the cut size and will leave the hydrocyclone for 95% via the underflow. The type of hydrocyclone used is Rietema's hydrocyclone. The sizing calculations for the hydrocyclone can be found in appendix 8.7.

Table 8.6: Dimensions and design variables of the hydrocyclone (S02)

| *Equipment dimensions and parameters* | |
|---|---|
| Diameter (m) | 0.383 |
| Length (m) | 1.92 |
| Diameter lignin particles (μm) | 250-400 |
| Cut size (μm) | 50 |
| Removal of lignin (%) | 95 |
| Underflow solid concentration (v%) | 46.4 |
| Pressure drop (bara) | 0.41 |
| Temperature (°C) | 72.9 |
| Purchased equipment cost (€) | 5600 |

### 8.2.7 Dryers (D01 and D02)

There are two dryers. Dryer D01 is used to dry the produced pulp to reach the product specifications. Dryer D02 is used to dry the lignin and thereby make the lignin suitable to be burnt in the furnace. In both dryers the remaining solvent is evaporated. The dryer type selected is for both streams the rotary steam tube dryer (see chapter 5). In this way the solvent is recovered. The necessary heat is delivered by condensation of steam. Low-pressure steam of 1.7 bara and 115 °C is used. The calculations were partially performed in Aspen and partially in Excel (see appendix 8.8).

Table 8.7: Dimensions and design variables of the dryers

| | *Pulp dryer (D01)* | *Lignin dryer (D02)* |
|---|---|---|
| Area ($m^2$) | 18.5 | 18.7 |
| $U_0$ $W/(m^2°C)$ | 2726 | 2726 |
| Duty (MW) | 1.83 | 1.88 |
| Feed temperature (°C) | 74 | 73 |
| End temperature (°C) | 83 | 83 |
| Number of tubes | 79 | 80 |
| Diameter of tubes (mm) | 25 | 25 |
| Purchased equipment cost (€) | 85,498 | 85,912 |

### 8.2.8 Distillation column (C01)

The column is simulated in Aspen. It is assumed that the heavy components don't influence the vapor liquid equilibrium of the water methanol mixture and that all other components leave the column at the bottom. The column doesn't have a regular reboiler and condenser. The distillate is compressed to 4 bara and therefore the temperature and the boiling temperature increase enough to use the condensation heat of the distillate in the reboiler. A distillation column with a regular reboiler and condenser would have a reboiler duty of 30.5 MW and a condenser duty of 29.9 MW. The calculations are explained in appendix 8.8.

Table 8.8: Dimensions and design variables of the distillation column (C01)

| *Equipment dimensions and parameters* | |
|---|---|
| Temperature top (°C) | 64.65 |
| Temperature bottom (°C) | 93.15 |
| Height (m) | 16.8 |
| Diameter top (m) | 5.23 |
| Diameter bottom (m) | 4.19 |
| Number of trays | 18 |
| Feed stage | 14 |
| Recovery of methanol (%) | 99 |
| Purchased equipment cost column (€) | 160,000 |
| Purchased equipment cost sieve trays (€) | 76,500 |
| Material of construction | Stainless steel |

### 8.2.9 Compressor

The compressor is needed to compress the top stream of the distillation column to 4 bara.

Table 8.9: Dimensions and design variables of the compressor (K01)

| *Equipment dimensions and parameters* | |
|---|---|
| Compressor duty (MW) | 5.11 |
| Efficiency | 0.72 |
| Outlet pressure (bara) | 4.0 |
| Inlet temperature ($^{o}$C) | 64.6 |
| Outlet temperature ($^{o}$C) | 183.4 |

### 8.2.10 Pumps

Most of the pumps are only used for transport. Pump P01 is also used to pressurize the solvent stream to the operating pressure in the extractor (33 bara). The power requirement of pump P01 is therefore by far the highest compared to the other pumps. Detailed calculations can be found in appendix 8.10.

Table 8.10: Specifications of the pumps

| *Pump number* | *$\Delta P_{total}$ (Bara)* | *Power (kW)* | *Purchased cost (€) (2002)* | *Number of pumps purchased* |
|---|---|---|---|---|
| P09 | 2.46 | 0.024 | 1,981 | 3 x 2 |
| P02 | 2.55 | 0.056 | 2,179 | 3 x 2 |
| P01 | 32.9 | 203 | 9,807 | 3 x 3 |
| P04 | 0.88 | 2.94 | 8,321 | 3 x 1 |
| P05 | 2.61 | 2.29 | 8,321 | 3 x 1 |
| P03 | 0.93 | 0.33 | 4,755 | 3 x 3 |
| P07 | 1.48 | 0.26 | 3,665 | 3 x 1 |
| P06 | 1.15 | 0.22 | 3,962 | 3 x 1 |
| P08 | 0.32 | 1.43 | 8,321 | 3 x 1 |
| P10 | 0.84 | 10.8 | 12,185 | 3 x 1 |

The following pump types are used:

- multistage centrifugal: P09, P02, P01
- single stage centrifugal (3500 rpm): P03, P04, P05, P06, P07, P08, P10

8.2.11 Heat exchangers

The heat exchangers have different functions:

- Cooling of process streams: E01, E06, E11
- Heating of process streams: E02, E03
- Condensing of process streams: E04, E05, E07, E08, E10
- Heat integration: E09

In E09 the top stream of the column is condensed and the bottom stream of the reboiler is evaporated. The dryers discussed in 8.2.7 could also have been placed in this section, because you could see them as evaporators.
A detailed example calculation is added in appendix 8.11.

Table 8.11: Summary of the data and calculated values for the heat exchangers

| *Heat exchanger or condenser* | *Heat duty [kW]* | *Heat transfer area [$m^2$]* | *Purchased Cost [€] (2002)* | *Steam/Cooling water [kg/s]* |
|---|---|---|---|---|
| E03 | 21990 | 251.5 | 145,335 | 11.87 (steam) |
| E01 | 715 | 12.2 | 15,034 | 9.50 |
| E02 | 4220 | 55.3 | 41,094 | 2.28 (steam) |
| E05 | 26150 | 641.1 | 210,485 | 347.55 |
| E07 | 1854 | 38.8 | 32,073 | 24.64 |
| E04 | 2839 | 68.8 | 47,108 | 37.73 |
| E08 | 1772 | 36.0 | 31,071 | 23.55 |
| E06 | 2374 | 116.2 | 67,154 | 31.55 |
| E09 | 30130 | 883.8 | 250,577 | - |
| E10 | 4545 | 86.9 | 55,127 | 60.41 |
| E11 | 1940 | 167.0 | 84,194 | 46.41 |

In a regular plant, heat exchangers are probably more often used for heat integration. In our case there isn't much heat integration possible. The extraction takes place at 190 °C and this requires the most heat, while most of the heat is recovered by condensing methanol at 65 °C. Heat exchanger E02 is somewhat different from the rest. This one is integrated in the feeder of the extractor. Moreover a slurry of wood chips and water passes through the tubes, whereas high pressure steam passes across the shell side

8.2.12 Fermentor

To convert hemicellulose to biogas four fermentors are needed. Most of the conversion to biogas takes place in the lowest compartment. The produced biogas creates a gas lift in the reactor and therefore water is transported upward through a riser. The biogas is separated at the top and the water returns through the downcomer to the bottom. Therefore this type of fermentor is called an internal circulation fermentor. The total volume needed for this type of digester is four times smaller than the volume needed when using a regular fermentor, because of retention of biomass. More detailed information about the fermentor and calculations can be found in appendix 12.

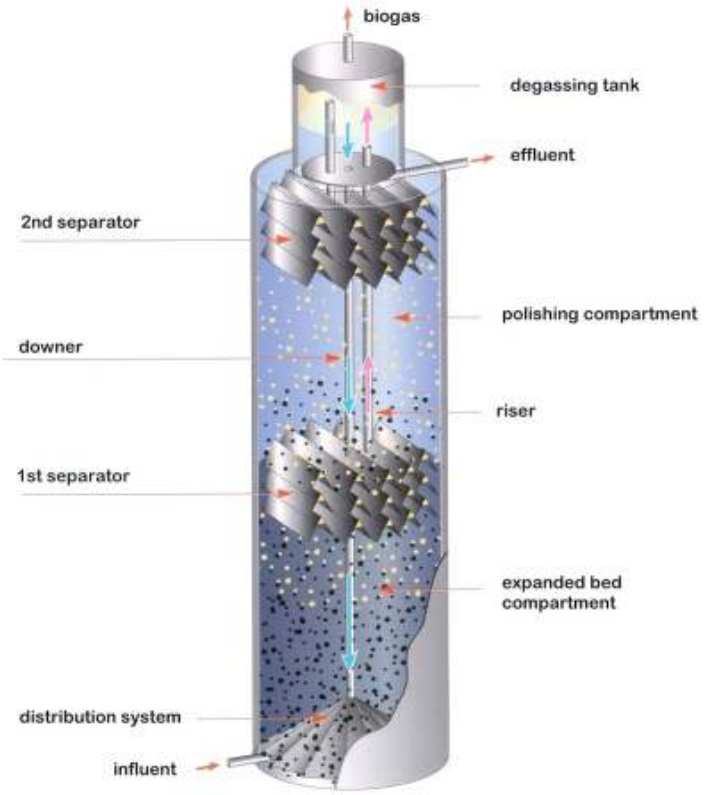


Figure 8.5: Internal circulation fermentor

The total volume needed is 8000 $m^3$. According to Mr. Mulder of Paques (ref. 133) the best configuration is four fermentors of 2000 $m^3$ with two settlers for biomass separation.

Table 8.8: Dimensions and design variables of the internal circulation fermentor

| *Equipment dimensions and parameters* | |
|---|---|
| Volume ($m^3$) | 2000 |
| Diameter (m) | 10.84 |
| Length (m) | 21.68 |
| Temperature (°C) | 40.2 |
| Pressure (bara) | 1.0 |
| Liquid residence time (day) | 0.96 |
| Material of construction | Stainless steel |

The total purchased equipment cost of the fermentors and the auxiliary equipment is 4,000,000 euro.

### 8.2.13 Furnace

A fluidized bed furnace is used to generate steam from lignin and biogas. The furnace contains two cyclones to separate the fly ash from the flue gases. The furnace produces steam of 50 bara superheated to 325 °C. Norske Skog Parenco in Renkum also uses this type of furnace. More detailed information and calculations can be found in appendix 8.13.

Table 8.13: Dimensions and design variables of the furnace

| *Equipment dimensions and parameters* | |
|---|---|
| Height (m) | 5.0 |
| Height of fluidized bed (m) | 0.8-2.0 |
| Lignin burnt (t/h) | 5.16 |
| Methane burnt (t/h) | 1.48 |
| Efficiency (-) | 0.75 |
| Temperature (°C) | 850 |
| Pressure of produced steam (bara) | 50 |
| Temperature of produced steam (°C) | 325 |
| Purchased equipment cost (€) | 4,720,000 |

## 8.2.14 Cooling tower

The cooling water is too hot to discharge directly and is therefore cooled in a cooling tower. Most problems with the cooling are encountered in the summer. The design is based on summer conditions. In the tower a large fan is used to blow air and increase the contact between air and the falling water. This sort of cooling tower is called a mechanical induced draft tower. Dimensioning of this tower can be found in appendix 8.14.

Table 8.14: Dimensions and design variables of the cooling tower

| Equipment dimensions and parameters | |
|---|---|
| Humidity (%) | 70 |
| Air temperature ($^{o}$C) | 16 |
| Wet bulb temperature ($^{o}$C) | 12.9 |
| Temperature of river water ($^{o}$C) | 20 |
| Temperature of water entering tower (°C) | 38 |
| Discharge temperature (°C) | 27 |
| Mass flow rate water (kg/s) | 581.35 |
| Total heat transferred (MW) | 26.7 |
| Area ($m^2$) | 125 |
| Purchased equipment cost (€) | 255,000 |

## 8.2.15 Storage tanks

*Storage tanks*

For the storage tank of methanol a storage capacity of 4 weeks is chosen. For process water a storage capacity of one day is chosen. The water make-up stream consists of the make-up stream for the solvent (stream <40>, 0.072 kg/s) and of the boiler feed water (1.783 kg/s). The methanol make-up stream<17> has a mass flow rate of 0.118 kg/s.

Table 8.14: Dimensions and design variables of the storage tanks

| Equipment dimensions and parameters | Water storage | Methanol storage |
|---|---|---|
| Make up stream water/methanol (kg/s) | 1.855 | 0.118 |
| Water needed in a day / methanol needed in 1 week (ton) | 160.3 | 71.4 |
| Volume of storage tanks ($m^3$) | 160.6 | 56.4 |
| Material of construction | Stainless steel | Carbon steel |
| Purchased equipment cost (€) | 112,600 | 50,300 |

# 9 Wastes

Wastes should always be avoided, if possible, from a sustainability point of view, but also for economic reasons. The re-use of solvents and unconverted reactants can be less expensive than the immediate disposal in waste streams. In our process the methanol will be recovered as much as possible. This will not only lead to lower costs due to a small make-up stream, but also to fewer methanol emissions to the environment.

Although we tried to produce as few waste as possible, there are still some waste streams leaving the process. For the CPD only direct wastes are considered. These waste streams can be found in table 9.1. The waste streams can be divided into three categories: solid, liquid and vaporous wastes. They will be discussed in this order.

Table 9.1: Waste streams

| *Stream* | *Amount (kg/s)* | *Main component(s)* | *Impurities* |
|---|---|---|---|
| Shives reject <12> | 0.083 | Shives | Water |
| Biomass <29> | 0.810 | Biomass | Water |
| Ashes | N/A | Ashes | |
| Waste water <38> | 7.420 | Water | Minerals, Methanol, Monosaccharides |
| Flue gases | N/A | Carbon dioxide, water | Ashes |

## *9.1 Solid wastes*

Solid wastes include shives reject from the screener, biomass from the fermentor and ashes from the furnace.

### 9.1.1 Shives reject

Chips leaving the steam explosion section that are not small enough leave the screener as rejects. A part of this stream is purged. This stream consists mainly of thick and lignin-rich pieces of wood, maybe some bark and knots. Because bark and knots are also present as waste in nature, the stream is harmless and no further treatment will be necessary. The shives stream cannot contain methanol, because the stream is already purged before the extraction takes place. The shives can only contain water as impurity, due to the steam added during the steam explosion, but water isn't harmful either. The shives stream might even be a profitable stream if it could be sold as land filling material used for recreational purposes, in parks or at playgrounds.

### 9.1.2 Biomass

The fermentor is designed in such a way that the main part of the biomass is kept inside, to avoid that the biomass is washed out and to keep the biomass concentration in the fermentor as high as possible. The outlet stream contains as much biomass as is grown in the fermentor. When the biomass has settled it will be thickened to 50% moisture content. The residence time inside the fermentor is calculated based on almost complete degradation of organics into biogas. According to H. Pasman (ref. 27) an acceptable organic concentration in the streams leaving the fermentor may not be higher than a Chemical Oxygen Demand of 100 ppm. The biomass stream

therefore contains only 2 ppm of methanol, 39 ppm of monosaccharides and 2.3 g/l minerals (see stream table).

The monosaccharides and minerals aren't harmful chemicals, but methanol is. For methanol the emission standard is a maximal concentration of 20 ppm (see ref. 108 and 109). In food even higher concentrations are allowed. For example in wine the maximum allowable concentration of methanol is 300 ppm (ref. 122). A concentration of 2 ppm of methanol therefore shouldn't be a problem.

Because the concentration of harmful or toxic substances will be low enough, it is possible to find an alternative use for this waste stream. If an offline analysis confirms the low methanol concentration, a possible function could be the use as additive to cattle feed, because of the mineral content.

#### 9.1.3 Ashes

In the fluidised bed furnace lignin and biogas are burnt to generate electricity. The three main components in the flue gases are carbon dioxide, water and fly ash. In the description of the furnace (see appendix 8.13) it is concluded that in our case toxic components such as sulphur compounds and hydrochloric acid won't be present in the flue gases, because the lignin and methane are clean fuels. The fly ash is separated from the flue gases by using two hydrocyclones. According to Mr. B. Kortekaas from Norske Skog Parenco this ash can be sold as an additive for concrete. This ash is known as pulp and paper ash.

### *9.2 Liquid wastes*

The only liquid waste stream in our process will be the stream leaving the fermentor section after the biomass has settled out. This stream contains minerals and a negligible amount of organics, due to the design specifications of the fermentor, which are coupled to the COD. The wastewater contains 4 ppm of methanol, 78 ppm of monosaccharides and 4.6 g/l minerals (see stream summary, appendix 5.4), which falls within the allowed range for emission standards (ref. 108 and 109).

We would like to return this mineral stream to the land where the trees are harvested or else to the riverbanks. The only restraint could be the flooding of the riverbanks. In case this occurs, the minerals will end up in the river instead of on the land. This shouldn't be a problem when the COD of the stream is lower than 100 ppm (ref. 27).

### *9.3 Vaporous wastes*

Only one vaporous waste stream leaves our process, which are the flue gases from the furnace. After the separation of the fly ash, only carbon dioxide and water will be present in this stream. Because the origin of the carbon dioxide is fast-growing biomass – i.e. willows – no net carbon dioxide will be discarded into the atmosphere; the fixation of carbon dioxide in biomass ensures a closed carbon cycle.

# 10 Process Safety

It is obvious that the design of a chemical process requires more than just a technical approach. Another aspect that has to be taken care of is a safety analysis of the process and the reduction of losses during operation. In the CPD two methods are used for identifying risk and improving safety. These are the Dow Fire & Explosion Index and a Hazard and Operability study (HAZOP). The first method provides a fast and systematic approach to identifying hazardous situations and to rank these areas accordingly. Based upon the results of the Fire & Explosion Index a second tool is used. Because not all the hazards (or interaction of hazards) may be discovered, a HAZOP is carried out on the most critical parts of the process. During the HAZOP a number of guidewords is used to reveal the process behavior when a deviation occurs in a process parameter. The whole process is a creative brainstorming session through interaction between team members. The HAZOP results in a better understanding of the process and measures that can be taken to reduce hazards.

## *10.1 Dow Fire and Explosive Index*

In order to determine the relative danger for a number of process units, a Fire and Explosion Index was determined for each of the units. The Dow Fire and Explosion Index was calculated using the 5th edition of the Dow Fire & Explosives Index Hazard Classification Guide (ref. 29). By reading the instructions it is a fairly straightforward process that needs to be carried out step-by-step. The result of the analysis is an indexing of the critical parts of the process and an estimation of business loss if an accident occurs in that part.

In our process we chose five process units that seemed the most feasible to examine from a safety point of view. It is also stated in the indexing guide that it is rarely necessary to calculate the F&EI for more than three or four process units. The units we chose are the methanol storage tanks, the steam explosion section, the extractor, the screw press and the separation column. The outcome of the analysis can be found appendix 10.2.

Because a complete discussion of every penalty would lead to a fairly tedious report, only the assumptions made during the analysis of the extractor will be given. The remaining numbers and factors for the other equipment can be found in appendix 10.1.

The first things to calculate are the material factor (MF) and the unit hazard factor ($F_3$).

- The material factor can be found in the appendices of the Hazard Classification Guide. The value for methanol is 16. The flammability value ($N_f$) is 3, which means that methanol is very flammable and has a low flash point. The reactivity value ($N_r$) is zero, because methanol is not reactive spontaneously under normal conditions. The health value is 1, which means that methanol is a low toxic chemical.
- The unit hazard factor is the product of the General Process Hazard Factor ($F_1$) and the Special Process Hazards ($F_2$).
- For the General Process Hazard Factor of the extractor the only penalty added to the base factor of 1 is because of the occurrence of a slight exothermic

reaction, namely the hydrolysis. For this reaction a penalty of 0.30 is added to sum up to 1.30 for the General Process Hazard factor $F_1$.

- The Special Process Hazards consist of penalties for:
  - the temperature (above boiling point, 0.60)
  - operation in flammable range (0.80)
  - pressure (35 bar relief pressure, 0.65)
  - the amount of hazardous substances (see fig.3 p.20: 1.95)
  - corrosion (slightly, 0.1)
  - the existence of rotating equipment (0.5).

  The Special Process Hazard Factor $F_2$ sums up to 5.60.
- The product of $F_1$ and $F_2$: $F_3 = 1.30 \times 5.60 = 7.28$. By multiplying this number with the Material Factor of methanol the Fire and Explosives Index can be obtained: F&EI = 7.28 x 16 = 117. A Fire and Explosives Index of 117 means an intermediate degree of hazard.

The next thing to do is to determine the damage factor based on the Material Factor (MF) and the Unit Hazard Factor ($F_3$) in fig.7 on p.27. This results in a damage factor of 0.64. The exposure radius is a linear function of the Fire and Explosion Index and equals in this case 97.8 (See fig. 8 on p.29). When a proper plant layout is available a direct cost estimate can be made of all the equipment within the radius of exposure (M€ 9.39). By multiplying this cost estimate with the Damage Factor the Base Maximum Probable Property Damage (MPPD) can be found. This product yields M€ 9.39 x 0.64 = M€ 6.01.

The second part of the F&EI is aimed at preventing damage and thereby reducing the risk. This is done by determining the Loss Control Credit Factors. There are three categories of loss control features, which have been assigned credits that can be applied to reduce the Base MPPD to an Actual MPPD:

- Process Control ($C_1$)
- Material Isolation ($C_2$)
- Fire Protection ($C_3$).

The product of all factors used in each category represents the credit factor for that category. The product of all three factors yields the Loss Control Credit Factor. Below an overview of the measures that should be taken to reduce the risk in the extractor.

Table 12.1 Contributions to the Loss Control Credit Factors in the extractor

| | | | |
|---|---|---|---|
| C1 Process Control | a | Emergency Power | 0.97 |
| | c | Explosion Control | 0.96 |
| | d | Emergency Shutdown | 0.96 |
| | e | Computer Control | 0.95 |
| | g | Operating Instructions | 0.865 |
| | h | Reactive Chemical review | 0.85 |
| C2 Material Isolation | a | Remote Control Valves | 0.94 |
| | c | Drainage | 0.85 |
| C3 Fire Protection | a | Leak detection | 0.97 |
| | f | Sprinkler system | 0.7 |
| | j | Hand extinguishers | 0.97 |

The product of the three factors yields 0.37. In fig.9 on p.31 the actual Credit factor can be found. This is 0.53. Now, by multiplying the Base MPPD with this Credit Factor the Actual MPPD can be found. In this case it is equal to M€ 3.19.

Finally the Maximum Probable Days Outage (MPDO) can be found in fig.10 on p.37. The estimation for the MPDO is 51 days. The Business Interruption Loss (BI) can be found by the following formula:

$$€BI = \frac{MPDO}{30} \cdot 0.70 \cdot €VPM \qquad (10.1)$$

with:
€BI = Business Interruption Loss in euros
MPDO = Maximum Probable Days Outage (days/year)
€VPM = Value of Product Manufactured (euros/month)
= amount of pulp produced (kilo per month) · price per kilo =

$$\frac{100 \cdot 10^6}{12} \cdot 0.55 = M€\ 4.56$$

In our case, the Business Interruption Loss for the extractor will be M€ 5.40.

This concludes the F&EI for the extractor.

An overview of the Fire and Explosion Index and the Business for the five investigated units will be given below.

Table 10.2 Overview of the results of the Fire & Explosives Index method

| *Process Unit* | *Unit Hazard Factor F3* | *Material Factor MF* | *F&EI (F3XMF)* | *Business Interruption Loss M€* |
|---|---|---|---|---|
| Steam Explosion | 3.38 | 1 | 3 | 1.01 |
| Extractor | 7.28 | 16 | 117 | 5.40 |
| Screw Press | 3.77 | 16 | 60 | 1.22 |
| Column | 3.50 | 16 | 56 | 1.75 |
| MeOH storage tank | 3.75 | 16 | 60 | 0.65 |

From this overview one can see that the Fire and Explosion Index for the extractor is the highest and indicates an intermediate hazard. The Business Interruption will be the highest if the extractor doesn't work anymore. The other discussed units only show a small hazard, with a lower Business Interruption. Therefore we will only make a HAZOP analysis of the extractor, because if this apparatus doesn't work the economic loss we be highest.

## *10.2 Hazard and Operability study*

Because the other units are classified as imposing a light degree of hazard, a HAZOP is performed on the extractor only. As would be expected, the biggest loss will be suffered when an accident occurs in this unit. One of the largest penalties imposed

upon the extractor is a result of the quantity of flammable material inside this unit. The only way to reduce this number is the economically unfavorable alternative of building several smaller units, which are separated from each other sufficiently. After performing a HAZOP (see appendix 10.3), we believe to have found a number of protective measures to decrease the degree of hazard in this unit. These alterations will be described next.

### *10.3 Recommendations*

Based upon the foregoing studies several measures can be taken to reduce the assessed risks. The required actions mentioned in the HAZOP will be clarified.

- Fail-safe control systems: the control system is designed in such a way that if the equipment fails or the electricity supply malfunctions, the valves assume a safe position.
- Buffer tanks: to prevent a total shutdown of the plant in case of a number of problems (too high or too low temperature of pressure, wrong solvent ratio) a buffer tank will be installed before the extractor. If the extractor doesn't work for a while, the stream from the steam explosion can be stored in a buffer tank. This prevents making an off spec product in the mean time.
- Pressure relief devices: in case of a too high pressure in the extractor the pressure can be relieved. The relief valves prevent a dangerous buildup of material and pressure. The vapor released by these valves, which contains mostly methanol and some water, will be sent to a flare.
- Alarm systems: if the temperature or the pressure in the extractor deviates too much from the set point, an alarm will sound. The operator may take the appropriate actions.
- Automatic shutdown-systems in case of an emergency: if a very hazardous situation exists (for example a methanol cloud due to a gas leak, which presents a risk to the plant personnel and the people who live in the area around the plant), an immediate shutdown will result. In this way the ignition sources are disabled and the plant will be evacuated.
- Water and sand to extinguish fires: Burning methanol should be extinguished with sand or with water spray. One cannot use a water jet stream, because the in this case the methanol would spread and a larger danger would be present. Because our plant is build next to a river, we can use the river water for the fire protection.
- Regular maintenance: regular maintenance decreases the chance of plugging, corrosion and controller malfunction.
- Larger capacity of process units: In case of disturbances in streams of equipment, the other equipment should be able to buffer. Therefore the capacity of the equipment should be a little higher than calculated. Also for critical pieces of equipment and auxiliary equipment a backup piece should be available, to prevent an immediate shutdown if just for example a pump doesn't work.

# 11 Economical Evaluation of the Plant

A cost estimation is done to evaluate the project. The profitability of the plant is assessed on the basis of the investment required and the cost of production. The lifetime of the project is estimated to be 20 years. Usually the plant life span is taken to be 10 years, however for plants of considerable sizes longer lifetimes can be taken. Especially in the pulp and paper industry, where factories have considerable dimensions, large investments are made for the plant. On the other hand these plants have a considerable lifetime.
The real lifetime of the plant is longer than the assumed 20 years, but within these 20 years the investment should be earned back. In these 20 years also the design and the construction of the plant is included, which is assumed to take approximately 2 years.
With the expected growth of the market for wood pulp in the foreseeable future (see appendix 11.1), the prospects for the plant are favorable.

First the Purchased equipment Cost, Fixed Capital Cost and Working Capital will be calculated, followed by the Operating Cost. With these values an Economic Evaluation of the project is made on the basis of several economic criteria. Also a sensitivity analysis is performed. The economic evaluation is mainly calculated according to chapter 6 of Coulson and Richardson's Chemical Engineering (ref. 14).

## *11.1 Purchased Equipment Cost*

The Purchased Equipment Cost (PEC) is the sum of all the equipment necessary in the plant. However the cost of equipment has been subjected to inflation. Therefore old cost data have to be updated to their present values.
An overview of the cost of the necessary equipment, the year of cost estimation and the Purchased Equipment Cost is reflected in the following table:

Table 11.1: Cost of necessary equipment and year of cost estimation

| *Type of Equipment* | *Year of cost estimation* | *Cost [€]* |
|---|---|---|
| Steam Explosion | 2002 | 6,000,000 |
| Screener | 2000 | 32,000 |
| Extractor | 2002 | 2,500,000 |
| Screw Press | 2002 | 500,000 |
| Flashes | 2000 | 153,300 |
| Hydrocyclone | 2000 | 5,600 |
| Dryers | 1998 | 171,410 |
| Phase Splitter | 2000 | 34,900 |
| Distillation Column | 1998 | 236,500 |
| Fermentors | 2002 | 4,000,000 |
| Cooling Tower | 2000 | 255,000 |
| Furnace | 2002 | 4,720,000 |
| Pumps | 2000 | 293,100 |
| Compressor | 1998 | 1,250,000 |
| Heat Exchangers | 1998 | 993,000 |
| Mixers, Buffer Tanks | 2002 | 30,000 |
| Methanol and Water Storage | 2002 | 162,900 |
| **Purchased Equipment Cost** | | 16,617,710 |
| **Purchased Equipment Cost** | **2002** | 16,617,000 |

With help of equation (A11.1.1), appendix 11.1 the equipment costs are converted to their present value. With these values the Total Purchased Equipment Cost in 2002 is calculated.
The total Purchased Equipment Cost is estimated at € 16,618,600. The price of the furnace is inclusive the cost for installation, piping etc. and therefore is not taken into account with the Purchased Equipment Cost. Especially the steam explosion section, the extractor, the fermentors and the furnace require a big investment.

### *11.2 Fixed Capital Cost, Working Capital and Total Investment Cost*

With the Purchased Equipment Cost, the Fixed Capital Cost and Working Capital of the plant can be determined. The Fixed Capital Cost is the total cost of the plant required for start-up. It includes cost of design, piping, instrumentation and control systems, buildings and structures etc.
Working Capital is the additional investment needed, over and above the fixed capital to start up the plant and operate it to the point when income is earned. It includes the cost of start-up, raw materials, finished product inventories etc.
Contrary to the Fixed Capital, most Working Capital is recovered at the end of the project.
The total investment needed for the project is the sum of the Fixed Capital Cost and the Working Capital

The Fixed Capital Cost can be calculated with the factorial method of Lang. The factorial method states that the Fixed Capital Cost of the project is a function of the Total Purchased Equipment Cost. The factorial method distinguishes between Direct Costs and Indirect Costs. By multiplication of the Purchased Equipment Cost with the appropriate Lang factors for fluids-solids, which can be found in ref. 14, p. 251, an estimation is obtained for the Fixed Capital Cost. The Fixed Capital Cost is inclusive the cost of the furnace. The Working Capital is estimated to be 5% of the Fixed Capital Cost. With the Fixed Capital Cost and the Working Capital the Total Investment Cost can be calculated. The results are summarized in the following table:

Table 11.2: Estimation of the Fixed Capital Cost and Total Investment Cost

| | |
|---|---|
| Purchased Equipment Cost | € 16,618,600 |
| Direct Costs | € 35,725,000 |
| Physical Plant Cost | € 52,342,000 |
| Indirect Costs | € 6,647,000 |
| Fixed Capital Cost | € 77,998,000 |
| Working Capital | € 3,900,000 |
| **Total Investment Cost** | € 81,898,000 |

The Total Investment Cost is relative large. However for plants with a large capacity, large investments are necessary. The price of equipment increases with the size of the equipment. Moreover to achieve a certain capacity, several equal equipment units have to be purchased. For example the steam section requires the purchase of two steam explosion units to process the amount of wood chips needed to fulfill the capacity of 100 kton/a cellulose pulp.

## *11.3 Operating Cost*

The Operating Cost is the cost for the production of the product. The Operating cost is divided into two groups:

- Fixed Operating Costs, costs that do not vary with the production rate. They have to be paid whatever the quantity produced.
- Variable Operating Costs, costs that are dependent on the amount of product produced.

An important Variable Operating Cost are the costs for raw materials and utilities. When the mass flow and the price of the raw material are known, the total Raw Material Cost can be calculated. The results are summarized in table 11.5.

Table 11.3: Total Raw Material Cost

| *Compound* | *Mass flow [ton/a]* | *Price [€/ton]* | *Cost [€/a]* |
|---|---|---|---|
| Wood Chips | 420,000 | 60.00 | 25,200,000 |
| Methanol | 3,398 | 208.00 | 707,000 |
| Water | 2,074 | 0.50 | 1,000 |
| Total Raw Material Cost | | | 25,908,000 |

The annual costs for methanol, which is the important solvent component during extraction, are quite small. Methanol is liberated from the wood during the extraction. Therefore relatively small amounts of methanol have to be supplied to the process and the mass flow and consequently the costs for methanol are small.

The only utilities that have to be bought are boiler feed water (BFW) and cooling water (CW). Electricity and steam are generated in the plant and therefore don't have to be purchased, whereas effluent treatment takes place in the fermentors. The wastewater that leaves the plant fulfills the requirements to be safely discharged without extra costs.

Table 11.4: Total Utility Cost

| *Compound* | *Mass flow [$m^3$/a]* | *Price [€/ton]* | *Cost [€/a]* |
|---|---|---|---|
| Boiler Feed Water | 51453 | € 0.50 | € 25,700 |
| Cooling Water | 16776433 | € 0.03 | € 503,300 |
| Total Utility Cost | | | €529,000 |

The total Operating Cost is estimated on basis of the Fixed Capital Cost, Direct Production Cost, Maintenance Cost and Operating Labor Cost. The total Operating Cost is summarized in the following table:

Table 11.5: Total Operating Cost

| Type of Cost | Comment | Cost |
|---|---|---|
| Total Raw Materials Cost | | € 25,908,000 |
| Miscellaneous Materials | 10% of Maintenance Cost | € 390,000 |
| Utilities | | € 529,000 |
| Total Variable Costs | | € 26,827,000 |
| Maintenance | 5% of Fixed Capital Cost | € 3,900,000 |
| Operating Labor | 3 shifts a day of 6 workers | € 810,000 |
| Laboratory Costs | 20% of Operating Labour | € 162,000 |
| Supervision | 20% of Operating Labour | € 162,000 |
| Plant Overheads | 50% of Operating Labour | € 405,000 |
| Capital Charges | 9% of Fixed Capital Cost | € 7,020,000 |
| Insurance | 1% of Fixed Capital Cost | € 780,000 |
| Local Taxes | 2% of Fixed Capital Cost | € 1,560,000 |
| Royalties | 1% of Fixed Capital Cost | € 780,000 |
| Total Fixed Costs | | € 15,579,000 |
| Direct Production Costs | | € 42,406,000 |
| Sales expense | | |
| General Overheads | 25 % of the Direct Production cost | |
| Research and Development | | € 10,601,000 |
| Annual Operating Cost | | € 53,007,000 |

The Direct Production Cost is the sum of the Total Variable Cost and the Total Fixed Cost

The term "Capital Charges' reflects the payback of the plant over the life span of the plant. The plant life span is taken to be 20 years. According to ref. 14 the Capital Charge can be taken as 2% above the current minimum lending rate. The present lending rate is about 7% and therefore the Capital Charge is taken as 9% of the Fixed Capital.
If the investment comes from a loan, this money can be used to repay the loan, including interest. In practice money for such an investment comes from internal resources and then the Capital Charge is an internal (book) transfer to reflect the cost of the capital used. This money can be set aside for new projects.
According to the table above the Raw Material Cost (consists mainly of cost for wood chips) forms the largest expense, followed by Capital Charges and Maintenance Cost.

The production cost of pulp in €/ton is equal to the Annual Production Cost divided by the annual production rate of cellulose pulp.

Table 11.6: Calculation of the production cost.

| | |
|---|---|
| Annual Production Cost | € 53,007,000 |
| Annual production rate | 116200 ton |
| Production cost | 456.14 €/ton |

The Production Costs are 456.14 €/ton, which is mainly caused by the high Raw Material Cost.

### *11.4 Gross Income and Net Cash Flow*

The Gross Income is equal to the Profit From Sales. The main product of the plant is the cellulose pulp, whereas the produced biogas is a byproduct. The selling price of pulp is based on the selling price of Kraft pulp. However the lignin content of Kraft pulp is lower than of our pulp. On the other hand our pulp has a lower hemicellulose

content than Kraft pulp, which may have a positive influence on the pulp selling price. Therefore the selling price of Kraft pulp is taken.
About two third of the biogas is burned to provide the energy for the plant. The remaining biogas is sold. The income from biogas is based on the production of methane and so the biogas price is also based on methane only, that is the produced carbon dioxide in the fermentor is considered worthless. The contribution of fertilizer, biomass and shives to the Gross Income is relatively small. In the following table the calculation of the Gross Income is reflected.

Table 11.7: Calculation of the Gross Income

| *Products* | *Price [euro/ton]* | *Price [euro/kg]* | *Mass flow [ton/a]* | *Revenues [euro/a]* |
|---|---|---|---|---|
| Pulp | € 550.00 | € 0.55 | 116200 | € 63,910,000 |
| Biogas | € 320.00 | € 0.32 | 6566.4 | € 2,101,000 |
| Fertilizer | € 150.00 | € 0.15 | 990 | € 149,000 |
| Biomass | € 35.00 | € 0.04 | 11640 | € 408,000 |
| Shives | € 60.00 | € 0.06 | 2390 | € 143,000 |
| Total | | | | € 66,711,000 |

The Net Cash Flow (NCF) is simply the difference between Gross Income and Operating Costs:

Net Cash Flow = Gross Income – Operating Costs (11.2)

The Annual Operating Cost is reflected in table 11.5, whereas the Gross Income is calculated in table 11.7. In the following table the Net Cash Flow is determined, according to equation (11.2).

Table 11.8: Calculation of the Net Cash Flow

| | |
|---|---|
| Gross Income | € 66,711,000 |
| Operating Costs | € 53,007,000 |
| Net Cash Flow (NCF) | € 13,704,000 |

The Net Cash Flow is positive, therefore the plant has an annual profit. The Net Cash Flow however is not a constant value. Its value changes, depending on the developments of the market of pulp and the price variations of the raw materials.
Compared to the Total Investment Cost the Net Cash Flow is relatively small. The Operating Costs are large, caused by the high Raw Material Cost (mainly the expenses for wood chips) and large Capital Charges due to the large Total Investment Cost. This small Net Cash Flow compared to the Total Investment Cost will lead to a long Pay Back Time of the plant.

## *11.5 Economic Criteria*

Various Economic Criteria are evaluated to determine the economic performance of the plant. With these criteria the economic performance of the plant is determined. The following economic criteria are considered:

- Rate of Return (ROR)
- Pay Out Time (POT)
- Maximum Total Investment Cost (MTIC)
- Discounted Cash Flow Rate of Return (DCFRR)
- Total Earnings

The Rate of Return is the ratio of the annual profit to total investments. The calculation of the Rate of Return is complicated by the fact that the annual profit (Net Cash Flow) is not constant over the life of the project. However the calculations assume a constant Net Cash Flow (calculated in table 11.8) over the lifetime of the plant.

The Pay Out Time is the time required after the start of the project to pay off the initial investment from income. It can be calculated from the Rate of Return.

The maximum amount of investments, which can be done before the plant is unprofitable, can also be calculated. At an interest of 10% the Total Investment Cost can be calculated, that makes the Cumulative Net Present Flow at the end of the product equal to zero. This Maximum Total Investment Cost is in our case equal to € 106,098,000.

Another important economic criterion that is calculated is the Discounted Cash Flow Rate of Return (DCFRR). This is the interest at which the Cumulative Net Present value of a project becomes zero, so this is the maximum interest a project can bear, before becoming unprofitable. The maximum interest the project can bear is found to be 14.1 %.

Finally the Cumulative Net Cash Flow at the end of the project, which is equal to the Total Earnings is determined. The Total Earnings of the plant after 20 years are equal to €159,285,000.

The economic criteria are summarized in the following table.

Table 11.9: Calculated economic criteria for the plant

| | |
|---|---|
| Rate Of Return (ROR) | 9.7 % |
| POT | 10.3 year |
| Maximum Total Investment Cost | € 106,098,000 |
| Discounted Cash Flow Rate of Return | 14.1% |
| Total Earnings | € 159,285,000 |

According to this table the Rate Of Return is relatively small, leading to a relatively large Pay Out Time. Typical Pay Out Times vary from 2 to 5 years. However for large plants, with large investment costs, longer Pay Out Times are more convenient. The large Pay Out Time is caused by the relatively small Net Cash Flow compared to the large Total Investment Cost.

The Maximum Total Investment Cost is approximately 130% of the Total Investment Cost. However the Total Investment Cost is an estimation and the real Total Investment Cost will deviate from this value. According to this table the real Total Investment Cost can deviate 30% from the estimated investment costs before the plant becomes unprofitable.

In the following graph a plot is made of the Cumulative Net Cash Flow versus the time. The Cumulative Net Cash Flow is based on the Cumulative Net Future Value.

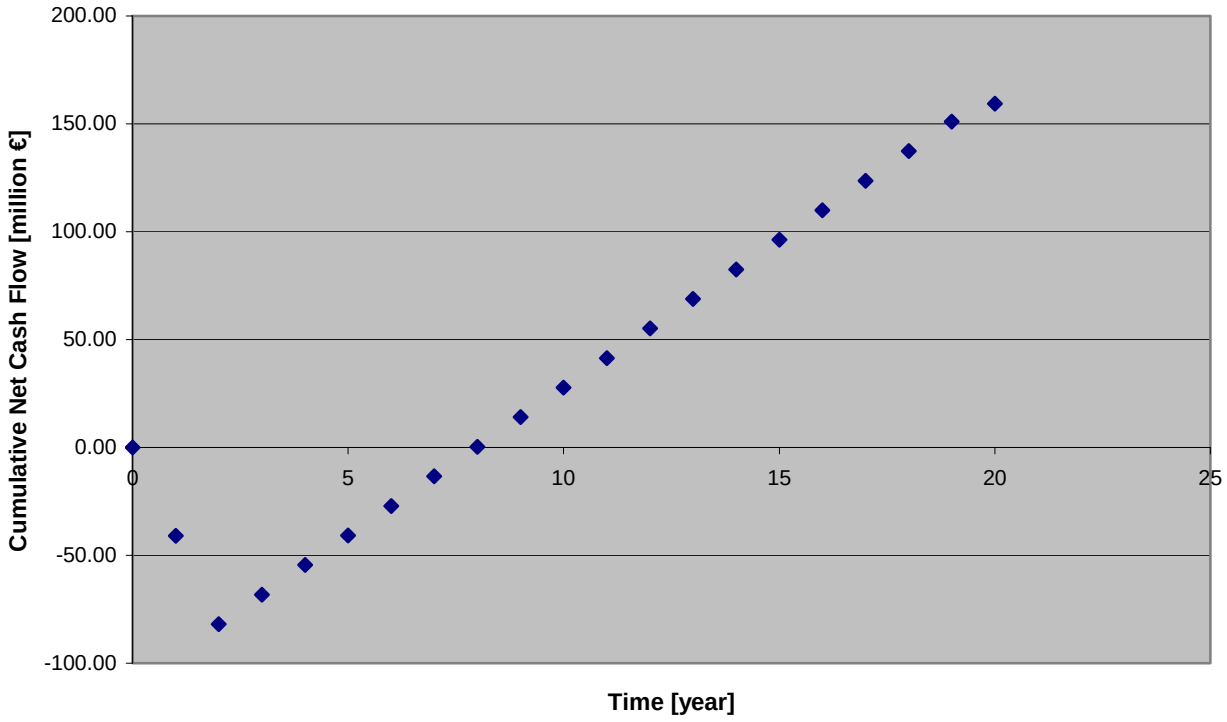


Figure 11.1: Cumulative Cash Flow versus time

In the first two years investments are made to design the plant and consequently build and start up the plant. Once the process is on stream income is generated from sales. The Net Cash Flow is positive, but the Cumulative Net Cash Flow is negative until the investment is paid off. In subsequent years the cumulative cash flow is positive. The project is earning a return on the investment. Towards the end of the project life the rate of cash flow decreases, due to increased operating costs (maintenance costs increases) and falling sale volumes (the plant is more often brought to a stand still, due to equipment failures).

## *11.6 Sensitivity Analysis*

The foregoing calculations were all made assuming constant prices for the raw materials and the products. However prices vary over periods, due to fluctuations in supply and demand. It is therefore important to examine how the plant is influenced by fluctuations in prices of raw materials and selling prices of products.

If one looks at the table of the Operating Costs the expenses for the wood chips stand out. The expenses for the wood chips are for approximately 48% part of the Total Operating Cost. It is therefore useful to determine what influence an increase or decrease in wood chip price has on the economic criteria. The price of the wood chips is therefore 10% increased and subsequently 10% decreased. The results are summarized in the following table.

Table 11.10: Sensitivity analysis for changes in price of wood chips

| *Economic criterion* | *Increase of 10%* | *Decrease of 10%* |
|---|---|---|
| Rate Of Return | 6.3 % | 13.1% |
| Pay Out Time | 15.8 year | 7.6 year |
| Discounted Cash Flow Rate Of Return | 10.0 % | 17.8 % |
| Maximum Total Investment Cost | € 81,710,000 | € 130,486,000 |
| Cumulative Cash Flow at the end of the project | € 103,845,000 | € 214,725,000 |

The economic criteria are very sensitive to changes in the price of wood chips. This is not surprising, because the wood chips make a large part of the Total Operating Cost, which consequently influence the Net Cash Flow. Especially the Total Earnings are strongly dependent on the price of wood chips. A decrease of 10% in the price of wood chips increases the Cumulative Cash Flow at the end of the project with 35%. Decreases in the price of wood chips are therefore very favorable for the plant, whereas increases are detrimental.

Another important component is methanol. Methanol doesn't form a big part of the Raw Material Costs, however it is subjected to large price fluctuations. Therefore the influence of methanol on the economic criteria is also determined.

Table 11.11: Sensitivity analysis for changes in price of methanol

| *Economic criterion* | *Increase of 10%* | *Decrease of 10%* |
|---|---|---|
| Rate Of Return | 9.6 % | 9.8 % |
| Pay Out Time | 10.4 year | 10.2 year |
| Discounted Cash Flow Rate Of Return | 14.0 % | 14.2 % |
| Maximum Total Investment Cost | € 105,414,000 | € 106,782,000 |
| Cumulative Cash Flow at the end of the project | € 157,730,000 | € 160,841,000 |

As was expected changes in the price of methanol don't have a big influence on the economic criteria. The methanol costs form only a small part of the total Operating Cost.

Pulp is the main product of the plant. The profitability of the plant is mainly dependent on the sales and the selling prices of the pulp. The selling price of the produced pulp is estimated at 550 €/ton. In the following table a sensitivity analysis is performed on changes in the pulp prices with 10%.

Table 11.12: Sensitivity analysis for changes in price of pulp

| *Economic criterion* | *Increase of 10%* | *Decrease of 10%* |
|---|---|---|
| Rate Of Return | 16.6 % | 2.9% |
| Pay Out Time | 6.0 year | 35.0 year |
| Discounted Cash Flow Rate Of Return | 21.4 % | 5.0 % |
| Maximum Total Investment Cost | € 155,579,000 | € 56,617,000 |
| Cumulative Cash Flow at the end of the project | € 271,767,000 | € 46,804,000 |

The impact of fluctuations in the pulp selling price is high. This is not surprising, considering pulp is our major product. Whenever the price of the pulp drops with 10% it is not very favorable anymore to build the plant, because than he Total Earnings at the end of the project are relatively small. However a decline in the pulp price is not expected (see appendix 11.2).

Table 11.13: Sensitivity analysis for changes in price of methane

| *Economic Criterion* | *Increase of 10%* | *Decrease of 10%* |
|---|---|---|
| Rate Of Return | 10.0 % | 9.5 % |
| Pay Out Time | 10.0 year | 10.5 year |
| Discounted Cash Flow Rate Of Return | 14.4 % | 13.8 % |
| Maximum Total Investment Cost | € 107,725,000 | € 104,471,000 |
| Cumulative Cash Flow at the end of the project | € 162,983,000 | € 155,587,000 |

The price fluctuations of biogas have little influence on the economic criteria. The amount of biogas that is sold is too low to have a large influence on the economic performance of the plant.

The accuracy of the equipment costs estimations is not high due to the fact that for important plant sections (steam explosion, extraction, furnace) no accurate information was available. Therefore the estimation for the Total Investment Cost is also not very accurate. A sensitivity analysis is performed by increasing and decreasing the Total Investment Cost with 10% to investigate the influence of the Total Investment Cost on the plant performance. In the following table the influence of these changes on the economic criteria is reflected.

Table 11.14: Sensitivity analysis for changes in the Total Investment Cost

| *Economic Criterion* | *Increase of 10%* | *Decrease of 10%* |
|---|---|---|
| Rate Of Return | 8.4 % | 11.4 % |
| Pay Out Time | 11.9 year | 8.8 year |
| Discounted Cash Flow Rate Of Return | 12.5 % | 15.9 % |
| Maximum Total Investment Cost | € 106,098,000 | € 106,098,000 |
| Cumulative Cash Flow at the end of the project | € 151,096,000 | € 167,475,000 |

The sensitivity of the economic criteria to a 10% increase and decrease in Total Investment Cost is relatively low, compared with for example the sensitivity of the criteria to fluctuations in the pulp or wood chip prices. The Total Investment Cost is very large and therefore a 10% change, has relatively little influence on the economic performance of the plant.

## *11.7 Subsidy*

The produced biogas can be used to generate green energy, that is energy that is obtained from the combustion of a renewable material. The biogas is obtained in a sustainable way from a renewable source: the biogas is produced by bacteria that convert hemicellulose to mainly methane and carbon dioxide. In the Netherlands the government provides subsidies to stimulate the generation of green energy. Perhaps the plant is qualified for the allotment of a subsidy. This subsidy will then be an extra source of income for the plant.

# 12 Creativity and Group Process Tools

## *12.1 Creative and group methods*

In the design process creativity is very important. Creative thinking leads to innovative ideas to improve the design. Moreover group methods are important for working in teams. To enhance creativity and to stimulate the use of creative and group methods, we were guided by our creativity coach, Hedzer van der Kooi.

Every week we had a creativity session with our coach. In these sessions we discussed about the problems that we met during the design. Some of these problems were technical problems, others were of social matter. With the technical problems, the coach stimulated us to think of alternative solutions, opposites of our ideas and to make a strengths and weaknesses analysis. The coach was also emotionally involved with the group. When two of the group members had had an accident he was concerned, but also he stimulated the other members to carry on with the project. When something didn't succeed, or when unexpected problems arose, he was our mental coach. He always gave us a positive impulse.

During the CPD-project we used the following creative and group methods (see paragraph 12.2 and appendix 12.1 and 12.2 for applications of these methods):

1. Knowing the group members (group profile)
   Within groups there can exist several manners of behavior. The group members, who work together, are dependent on each other. They have the same goal: finishing the project with a satisfying result. Working in teams is impossible if nobody cares about the other team members, or if no agreements and planning are made. In these cases no good result can be achieved. The only way of satisfyingly working in teams is by mutual control of behavior. This means that the team members tell each other the truth, know each other's strengths and weaknesses and take this into account. Only in this way a positive result is achieved. Therefore we made a strengths and weaknesses analysis of each team member and combined this to a group profile. The strengths are exploited by making a subdivision of the tasks (each team member performs tasks he/she is good at) and the weak points are improved by acknowledging them and trying to do something about it (see appendix 12.1: what to do with our weaknesses). The team members help each other with their weak points.

2. Knowing more about other team members
   It stimulates team building if the team members also see each other at moments when they are not working on the CPD project. This improves the atmosphere between the team members. Although we knew each other quite well already (as class mates), we learned new things about each other (personal, as friends). Now we are really friends. Also two of the team members have a relation with each other. The motivation and the pleasure in working for the CPD project increase when one is familiar and friendly with the other team members. Examples of team building are having diner together at one of the team member's home, go to a pub and drinking a beer together and going out together.

3. Self-reflection and analysis of own behavior
   In the CPD project it is important that you are not only critical towards the ideas of others, but also towards your own ideas. You should be able to self-reflect to really see the best option and to make the right decisions.
   When working with other team members, it is important that the team members get on well together. Problems and quarrels can be prevented by analysis of the influence of the own behavior on the response of the other members. You have to look at the reaction of the other team members on your attitude. In this way one can learn how to go about specifically with each team member. Moreover a reliable and open atmosphere is created, in which everybody feels free to talk and give a response without the fear of saying something stupid or the fear of facing many critical questions.

4. Spontaneous ideas
   The first creative method is to get a spontaneous idea. Drs. D. Grunwald calls this a brainwave. These spontaneous ideas can arise during the creativity sessions with our coach, but also every other minute, especially when you are not thinking about the specific problem in the project. This can be in lunch breaks, in the train or at home. Most of the time a brainwave arises when you are relaxed. The course instructor already foresaw that spontaneous ideas don't always arise when you are sitting behind the computer and therefore we got a blue notebook to write down spontaneous ideas. In this way we couldn't forget them. This works in the same way as with dreams, when you just got awake, you know exactly what you dreamed. However a few minutes later you have forgotten it completely.

5. Trying to think of more alternatives (opposites of options)
   When you face a problem, you look for solutions. Most often the first solution that you think of is the most convenient solution. We tried to think of more alternative solutions, for example by looking at the opposite of the first solution, even if you have never heard of such a solution. The more options you can think of, the better the choice that is finally made. In this way no solutions are left out.

6. Comparison of the options (strengths and weaknesses)
   To choose the best option out of all alternatives, a strengths and weaknesses analysis is made. By putting plusses and minuses in a table with selection criteria an overview of the options is obtained. The best option is the option with the most plusses. If two options have the same outcome, the selection criteria have to be weighed and the option which is most positive at the most important selection criterion that is chosen.
   When one team member has written about the options in a step, he/she presents the findings on the blackboard and tells the other team members about the advantages and disadvantages of the different options. After this presentation the other team members are encouraged to critically ask questions about the different options and also think of the best option. All arguments used have to be well based. Then everybody votes for the best option in his own view and only when everybody agrees a possibility is chosen. In this way the decision is made about important issues.

We stimulated each other not to agree immediately with an option, but to look critically at it and to ask critical questions. Our coach was also good in asking critical questions. We stimulated each other only to agree, when you believe the person is right and not because one fears to answer critical questions if he/she doesn't agree.
When not everybody agrees in the final decision, a discussion is held. This means a conflict between personal (own idea is the best) and group interest (we search the best option). The best solution is to negotiate and strive for the best solution for the whole group (long-term vision). The team members should be able to self-reflect (see point 9), seeing also the weaknesses of their own ideas, even if they are very excited about it.
In conflicts in choosing the best option most of the time more information was needed to make the final decision. In that case one team member searches for new or more information and subsequently a new presentation with voting session is held.

7. Development of an idea by integrating the ideas of different team members
   To develop an idea we used the following method in the creative sessions: The first team member tells his/her idea and the advantages and disadvantages to the other team members. The other team members add their ideas to the original idea. In this way the knowledge of all team members is combined and the first idea is extended and improved.

8. Use of imagination (visualizations)
   To imagine how for example something works, the best way is to visualize the object. In this ways one compares an undefined object with a defined one, of which you know exactly how it looks like or how it works. It is easier to talk about difficult matters if you have something to compare it with.
   Imagination can also be used to come to ideas that are not conventional. Within your fantasy everything is possible. Our coach stimulated us not to be afraid of saying something that comes up in your mind although you don't know if it is realistic or possible. The best option is not always convenient.

9. Use of drawings to illustrate ideas. To visualize a process option, the best way is to draw it on the blackboard. In this way all the team members understand the option better. The drawing can illustrate the ideas. Different flow sheets were drawn on the blackboard in our room. After we all read about one process option, we all drew our idea of this option on a paper and compared each other's interpretations.
   We also did a brainstorm session about the possible byproducts with the help of drawing instead of writing the idea. Instead of writing what to do with the lignin and hemicellulose, we drew the applications. This way of brainstorming, which is called brainsketching, leads to more associations and creative ideas.

During the CPD-project the following issues don't lead to creativity:

1. We think checklists do not enhance creativity, because these leads to systematical thinking and not creative thinking. It is not creative to look at a list and see what you have to do, instead of thinking for yourself what you

should do. Although systematic thinking isn't creative, it does help to obtain an overview. For example the planning we made was very systematic.

2. Creativity is neither enhanced by a too well defined assignment. The CPD-assignment should be an open assignment as much as possible, where several solutions are possible. Thinking of more options and solutions and to choose the best one is a creative process.

3. We also think it is not creative to use only 'proven technology'. This never leads to new creative and original ideas. We understand that a firm doesn't want to take too much risk and therefore uses proven technology (if a process is not proven, it may not be working and economically feasible), but if nobody ever tried something new, the industry wouldn't have developed at all. We do understand that most steps in the process should be 'proven'. In the CPD project, creativity is therefore seen as looking at all the options you can think of (proven options as well as new ones) and choose the best one out of it, even if the best option is not original at all.

### *12.2 Overview of the creative and group methods used during the CPD project*

23 September 2002:
- 9.00 h: We were given the assignment for the CPD project, read it and searched for the patent of the Alcell process
- 15.00 h: In the afternoon we had our first creative session about the creativity articles. We discussed the creative methods in the articles and determined which creative and group methods we could use in our design: brainsketching & brainwriting, spontaneous ideas at relaxed moments (we hope we have them), open atmosphere between team members, combining knowledge and analysis of own behavior.

24 September 2002:
- 13.30 h: First visit of our coach and creative session. We discussed about the expectation of the group members of the CPD project and what we thought of the assignment. We expect that it is just like the first and second years project. Everybody started with a positive attitude towards the project and expected that we are able to finish the project with a good result. Although we have to work hard, we think we also have time for informal activities.

27 September 2002:
- 10.00 h: Kick-off meeting: During the kick-off meeting a lot of questions about the process itself and about creative methods were answered. We asked the principle how far we could deviate from the Alcell process, why willow wood was chosen for the production of pulp and in which degree the plant should be self-sufficient. We also talked about the articles about creativity. We discussed about the contents of these articles and about what we had learned from these articles. We also had to think of what creative methods we are going to use in the CPD project. Afterwards we discussed about the things said during the Kick-off meeting and we arranged a weekly meeting with our coach every Monday afternoon.

30 September 2002:

- 9.30 h: Creative session with our coach: Which byproducts will we make? What to do with lignin: burn or find market for it? What to do with hemicellulose: make ethanol, furfural or xylitol? Bianca had a spontaneous idea: lactic acid (for making of bioplastics). In the brainstorm session about the possible byproducts and what to do with them, we used drawings of the applications (brainsketching).

1 October 2002:

- 13.30 h: Personal strengths and weaknesses analysis. Everybody mentioned 4 personal strengths and 4 personal weaknesses. We combined these personal profiles to a group profile (see appendix 12.1). We decided to have a session about what we should do with our weaknesses.

4 October 2002:

- 10.00 h: We generated options for the Basis of Design: such as a pretreatment with fungi or not, the mode of extraction (is opposite of batch-wise Alcell process also possible?), use of catalyst or not, extraction of all organics except cellulose as in the Alcell process, or the opposite (extract only the cellulose) and the order of recovery of lignin and hemicellulose. We decided we needed more information before determining which option we will choose.

7 October 2002:

- 10.00 h: Maaike had had a brainwave in the weekend: the separation of hemicellulose and lignin doesn't have to make use of cooling, in which lignin will precipitate, but can be done with a mesoporic structure. In this way the hemicellulose can specifically be hydrolyzed and at the same time be separated from the lignin, which will not pass through the mesoporic structure and will not hydrolyze. We made contact about this possibility with Dr. K. Janssen of Applied Organic Chemistry and Catalysis.
- 13.30 h: Creative session with our coach: we thought of how to continuously add wood chips at 40 bar. We made up ideas of solving this problem, for example using a special feeder, a hopper, a press, a pump, a conveyor belt, etcetera. Although some of the options are impossible to use for pressurizing chips, we stimulated each other to think openly and to say all ideas that come into your mind.

  We also drew process options on the blackboard, to get a better idea of the possible options, and showed them to each other. We determined advantages and disadvantages of several options.
- 16.00 h: To visualize the solubility and viscosity of hemicellulose, we put lumps of sugar in hot water till saturation was reached. After we had put more than 200 g into 100 ml water it still wasn't saturated. Then we cooled the solution slowly and the solution became viscous.

10 October 2002:

- 9.30 h: After we had made the group profile, we decided to have a session about what to do with our weaknesses. This analysis can be found in appendix 12.1. We also thought of other important aspects that are important when you work in groups: humor, dealing with the unknown, oral skills (discussions, presentations), criticism, enthusiasm, endurance, linguistic skills in English and flexibility (no 9.00 h to 17.00 h mentality).

11 October 2002:
- 9.00 h: Brainstorm session about the conversion of hemicellulose to valuable byproducts. We made a strengths and weaknesses analysis of the possible options. We eventually choose to produce lactic acid, because in this way only one byproduct is formed, which is very valuable, also in the future (good prospects for bioplastics). Therefore we need to know how to separate lactic acid from water.
- 13.30 h: Creative session about the separation of lactic acid and water. The only possibility we came up with was an extraction. Therefore we searched in literature for more options.
- 16.30 h: We came together and discussed the options found: ion exchange adsorption, electro dialysis, extraction and reactive extraction.

16 October 2002:
- 9.30 h: Talk about BOD report with the coach. What are the good points and what are the bad points. Where do we have to put emphasis on in the BOD presentation during the preliminary BOD meeting for tomorrow?

17 October 2002:
- 13.30 h: BOD meeting. During the BOD we got another point of view on the design so far. This new view was that the byproducts formation had to be 'proven', because the Alcell technology itself is already an uncertainty. Therefore we had to search for a more robust and proven conversion of the hemicellulose. This means that we are less free in the assignment than we first thought. However it gave us a new stimulus in creativity in designing the cellulose production plant. We had the feeling we learned a lot from the BOD meeting and we felt inspired by it.

18 October 2002:
- 9.30 h: Evaluation of the BOD review meeting. How do we go on from here? Lactic acid is not seen as a good option anymore: we will search for a more robust and proven process, such as the biogas production

21 October 2002:
- 9.30 h: Peter had the idea of stopping the conversion of hemicellulose to biogas halfway, for example at the moment that the organic acids are formed. We went to Prof. Dr. Ir. Heijnen and Dr. Jongejan for more information about this idea.
- 13.30 h: Creative session with coach about the hemicellulose use. We made a strengths and weaknesses analysis of the following options: furfural/ethanol, lactic acid, bio-diesel, furfural/lactic acid, hydroxyacids, ethanol and biogas. The following selection criteria were used: value of byproducts, proven technology, waste, costs, complexity and necessary purity. Eventually we choose to produce biogas.

23 October 2002:
- 15.30 h: Creative session about flow sheet. We draw different flow sheets on the blackboard. Furthermore we thought about what to do with cellulose losses during extraction. Will we recover it (how), or will we convert it together with the hemicellulose. This is easier, but cellulose has a higher value than biogas. We choose not to recover the cellulose, because this can only be done with a

mesoporic structure and the recovered cellulose has a too low molar weight to be used as pulp. We made a new planning and allocation of tasks for this week: searching why methanol/water ratio = 80/20, integration of solvent recovery equipment and how does a steam explosion work exactly.

28 October 2002:

- 13.30 h: Creative session with coach about the possible pretreatment steps. We made a strengths and weaknesses analysis of the use of fungi, refiner and steam explosion. We compared residence time, costs, pulp quality, safety, proven technology, environment and complexity of the different options and eventually we choose the steam explosion.

31 October 2002:

- 12.00 h: We wondered what the pulp would look like after the steam explosion, because this determines the type of extractor needed. Vincent visualized the pulp stream by comparing it with potting compost.

1 November 2002:

- Maaike had the following spontaneous idea: it is not necessary to wash the pulp after the steam explosion, because this is possible after the extraction too, it saves a lot of water and the acetic acid that is formed during steam explosion is sent to the extractor too (acts as a catalyst).

4 November 2002:

- 9.30 h: To visualize the process we wanted to visit a pulp factory. Warbout made contact with Parenco. We made a questionnaire for the firm with important questions we wanted to ask them so they would have an idea of what we wanted to know.
- 13.30 h: Creative session about mode of contacting of continuous extraction: cocurrent or countercurrent.
- Visualization: Maaike had brought a branch of willow wood. We made this branch in smaller pieces and put these in a bucket of water to see if the wood would sink or float. The willow wood floated for 3 days and thereafter sunk to the bottom. From this experiment we concluded that pulp is only heavier than water if it is totally saturated with water.

7 November 2002:

- 13.30 h: Session for analysis of group process. Is everybody satisfied with the cooperation between the team members? Does everybody work hard enough? Are we satisfied with the results achieved so far? What is the role of every person in the group? Is the communication between the team members good? We told each other the truth, but in general everybody thought the cooperation was very good. After the session the team spirit was enhanced with a drink and a chat together.

11 November 2002:

- 9.00 h: Brainstorm session about the process flow sheet. We discussed about the order of the equipment, for example if we should place the screener before or after the extractor. We also made a strengths and weaknesses analysis of the separation of the pulp and solvent and the lignin and hemicellulose solution. We drew all the options of the flow sheets on the blackboard to understand the options better.

- 14.00 h: Vincent makes pulp himself by chewing on paper and putting small pieces of paper in water. In this way he wanted to visualize what pulp looks like.

18 November 2002:
- 13.30 h: Creative session with our coach. During the construction of the energy balance and heat integration we had the spontaneous idea of using the amount of heat that is produced in the condenser in the reboiler. Therefore the top stream must be heated. How is that possible? We thought of heat exchangers and our coach came up with a compressor. We thought this was a very good idea and worked this out further with our own ideas. We drew a new scheme of the distillation column on the flip-over to visualize this option.

21 November 2002:
- 9.00 h: Based of the flow sheet we determined the necessary pumps and heat exchangers (use of drawings for better understanding and visualization) and thereafter calculated them

26 November 2002:
- Visit to Parenco, a pulp factory in Renkum for better understanding of a pulp factory (see appendix 12.2 for excursion report). Especially the screw press, the furnace and the conveyor belts, which we will also use, were quite interesting and helped us with the visualization of our own process.

27 November 2002:
- 10.00 h: Making of plant-layout by means of cutting pieces of cardboard as visualization of the pieces of equipment on scale. Different options for the layout could be made and a good one was chosen.

28 November 2002:
- 9.30 h: Safety and control analysis. Our process was already drawn on the blackboard. In this flow scheme we drew controllers at places were this was necessary. Everyone drew one by one on the blackboard the additional controllers that he/she missed and finally a total control system was made.

29 November 2002:
- 9.30 h: HAZOP analysis over the extractor. Together we asked questions like: what if the temperature or the pressure is wrong (too low or too high), what if the solvent ratio is wrong, et cetera. In this way we determined with our complete team what the hazards of the extractor are and what to do about it to minimize the risk

2 December 2002:
- 13.30 h: Last creative session with our coach. He wished us good luck in writing the report and we determined to have an evaluation of the total CPD project after we have handed in the report and had our final meeting. Then we will evaluate the problems we met, how we solved them, the use of creative sessions and creative methods in solving and the working in a team together with our coach.

# 13 Conclusions and Recommendations

Our objective was to design a plant that produces cellulose out of willow wood chips, by using Alcell technology. At the end of this report we will summarize the most important strengths and weaknesses of our design and we will provide recommendations.

The major strenghts of our design are the facts that the design is economically feasible and the plant is sustainable. The economic situation can improve by applying for subsidies for the production of biofuels. Besides the use of methanol no further toxic chemicals are used. The produced waste streams can be disposed off in an environmentally friendly manner. The plant is self-supporting in energy, which means that no energy from the outside is needed.

The major risk of the design is the Alcell technology itself. Because the Alcell process has never been succesfully commercialized, the technology is not proven. Moreover the kinetics of delignification are hardly known. A first recommendation therefore will be a thorough clarification of the kinetics. This is also true for some of the thermodynamic properties of willow wood.

The product has a lower quality than the Kraft pulp. The amount of lignin in the pulp is about twice as high and the molar mass of cellulose is lower.
Although delignification in the extraction poses no problems, the major issue is that it is difficult to separate the pulp and the solvent, which contains dissolved lignin, from each other. The pulp can only be thickened to 50% moisture content by means of a liquid-solid separation. The remaining solvent is removed by evaporation, which causes the dissolved lignin to precipitate. To improve the pulp quality a good suggestion would be to implement several washing stages after the extractor. First a washing step with methanol should wash out the lignin, continued by a washing step with water to recover the methanol and to prevent methanol emissions.
The molar mass of the pulp is lower, because we carry out a steam explosion before extraction. On the contrary the product quality is improved because the hemicellulose is removed much better and the extraction is not diffusion limited anymore.

We realize that methanol at high pressures can provide potential hazards. We think we made the right decision to use methanol as a solvent. A Hazard and Operability Study has been performed on the extractor to make sure that a safe working environment can be ensured. To minimize the risks we decided to design the remaining part of the process at atmospheric pressure.

## List of Symbols

| | | |
|---|---|---|
| $\beta$ | = | Device specific screening index (-) |
| $\Delta_r H$ | = | Enthalpy of reaction (kJ/mole) |
| $\Delta H^{vap}$ | = | Heat of evaporation (kJ/mole) |
| $\Delta H^{sub}$ | = | Heat of sublimation (kJ/mole) |
| $\Delta P$ | = | Pressure difference ($N/m^2$) |
| $\Delta P_f$ | = | Pressure drop due to friction ($N/m^2$) |
| $\Delta T_{lm}$ | = | Log mean temperature difference (°C) |
| $\Delta T_m$ | = | Mean temperature difference (°C) |
| $\eta$ | = | Efficiency (-) |
| $\phi$ | = | volume fraction of solids (-) |
| $\Phi_m$ | = | Mass flow (kg/s) |
| $\Phi_v$ | = | Volume flow ($m^3/s$) |
| $\mu_i$ | = | Viscosity of component i (Pa·s) |
| $\mu_r$ | = | Relative Viscosity |
| $\mu^{max}$ | = | maximum growth rate ($h^{-1}$) |
| $\rho_i$ | = | Density of component i ($kg/m^3$) |
| $\omega$ | = | Acentricity factor (-) |
| | | |
| A | = | Area ($m^2$) |
| A | = | Antoine coefficient (-) |
| B | = | Antoine coefficient (kJ/kmol) |
| $c_r$ | = | Concentration of rejects in reject stream ($kg/m^3$) |
| $c_f$ | = | Concentration of rejects in feed stream ($kg/m^3$) |
| $c_p$ | = | Specific heat capacity (kJ/kg°C) |
| C | = | Constant cost (€) |
| C | = | Antoine Coefficient (K) |
| $C_e$ | = | Purchased equipment costs (€) |
| $C_s$ | = | concentration of substrate (g/l) |
| $C_{s,min}$ | = | minimal substrate concentration, otherwise the micro organisms die (g/l) |
| $C_t$ | = | Throughput rate (kg/s) |
| $C_u$ | = | Unit capacity ($kg/s/m^2$) |
| $d_o$ | = | Tube outside diameter (m) |
| $d_i$ | = | Pipe inside diameter (m) |
| D | = | Diameter (m) |
| D | = | Diffusion constant ($m^2/s$) |
| $D_0$ | = | Diffusion constant at infinite temperature ($m^2/s$) |
| $D_i$ | = | Inlet equivalent diameter (m) |
| $D_o$ | = | Overflow diameter (m) |
| $D_u$ | = | Underflow diameter (m) |
| $E_a$ | = | Activation energy (J/mol) |
| E | = | Relative rougness (-) |
| ER | = | Screening efficiency (-) |
| Eu | = | Euler number (-) |
| f | = | Friction factor (-) |
| $F_\infty$ | = | Open-area factor (-) |
| $F_s$ | = | Slotted-area factor (-) |

$F_t$ = Temperature correction factor (-)
$g$ = Acceleration due to gravity (= 9.81 $m/s^2$)
$h_o$ = Outside fluid film coefficient ($W/(m^2°C)$)
$h_i$ = Inside fluid film coefficient ($W/(m^2°C)$)
$h_{od}$ = Outside dirt coefficient (fouling factor) ($W/(m^2°C)$)
$h_{id}$ = Inside dirt coefficient ($W/(m^2°C)$)
$H$ = Height (m)
$H_f$ = Enthalpy of formation (kJ/mole)
$K$ = Reaction constant ($s^{-1}$)
$k_o$ = Reaction constant at infinite temperature ($s^{-1}$)
$k_w$ = Thermal conductivity ($W/(m^2°C)$)
$K_p$ = Empirical constant (-)
$K_s$ = half-saturation constant (g/l)
$L$ = Length (m)
$m$ = mass flow-rate (kg/s)
$n$ = Index for the type of equipment (-)
$n_p$ = Empirical constant (-)
$N_f$ = Flammability value (-)
$N_h$ = Healt Value (-)
$N_r$ = Reactivity (-)
$N_{tube}$ = Number of tubes
$M$ = Molar mass (g/mole)
$P$ = Pressure ($N/m^2$)
$Q$ = Heat transfer per unit time (W)
$Q$ = volumetric feed flow rate ($m^3/s$)
$r$ = Radius (m)
$R$ = Universal gas constant ($kJ/(mole \cdot K)$)
$R_0$ = Explosion severity (-)
$Re$ = Reynolds number (-)
$R_f$ = Liquid underflow-to-throughput ratio (-)
$RR_m$ = Mass reject rate (-)
$t$ = Time (s)
$t_i$ = Temperature of stream i, tube-side (°C)
$S$ = Characteristic size parameter ($m^2$)
$Stk_{50}$ = Stokes-50 number at the cut size (-)
$T$ = Temperature (°C, K)
$T_c$ = Critical temperature (K)
$T_i$ = Temperatue of stream i, shell-side (°C)
$T_n$ = Normal boiling point (K)
$T_r$ = Reduced temperature (-)
$T_{sat}$ = Saturated temperature (°C)
$u$ = Fluid velocity (m/s)
$U$ = Overall heat transfer coefficient ($W/(m^2°C)$)
$V$ = Volume ($m^3$)
$V_r$ = Volumetric flow rate of reject stream ($m^3/s$)
$V_f$ = Volumetric flow rate of feed stream ($m^3/s$)
$w_i$ = Mass fraction of component i (-)
$W$ = Work done (J/kg)
$x$ = Solubility (g/g)
$x_{50}$ = hydrocyclone cut size (μm)

| | | |
|---|---|---|
| $Y_{sx}$ | = | Yield of biomass on substrate (g/g) |
| z | = | height (m) |

## Literature

*Books*


1. C.J. Biermann, Handbook of Pulping and Papermaking, 2nd ed., Oregon State University, USA (1996)

2. A. Blazej, M. Kosik, Phytomass, a Raw Material for Chemistry and Biotechnology, Ellis Horwood series, Bratislava, Slovakia (1993)

3. J.C.F. Walker, Primary Wood Processing, Principles and Practice, 1st ed., London (1993)

4. J.P. Casey (Ed.), Pulp and Paper, Chemistry and Chemical Technology, 3rd ed., New York, USA (1980)

5. R.A. Young, M. Akhtar, Environmentally Friendly Technologies for the Pulp and Paper Industry, Wisconsin, USA (1998)

6. K.W. Britt (Ed.), Handbook of Pulp and Paper Technology, New York (1964)

7. D.W. Reeve, Kraft Recovery Operations Seminar, TAPPI Press, Atlanta, USA (1987)

8. M.J. Kocurek, C.F.B. Stevens, Pulp and Paper Manufacture, Properties of Fibrous Raw Materials and their Preparation for Pulping, 3rd ed., TAPPI, Atlanta, USA (1983)

9. W.E. Scott, J.C. Abbott, Properties of Paper, An Introduction, 2nd ed., TAPPI, Atlanta, USA (1995)

10. C. Schuerch, Cellulose and Wood, Chemistry and Technology, New York (1989)

11. K.E.L. Eriksson (Ed.), Biotechnology in the Pulp and Paper Industry, Berlin, Germany (1997)

12. G.A. Smook, Handbook for the Pulp and Paper Technologists, TAPPI, Atlanta, USA (1982)

13. J.M. Douglas, Conceptual Design of Chemical Processes, McGraw-Hill Book Company, USA (1988)

14. R.K. Sinnott, Coulson&Richardson's Chemical Engineering 3rd ed., Butterworth-Heinemann, Oxford (2000)

15. G.J.M. de Koning, Prospects of Bacterial Poly[(R)-3-Hydroxyalkanaoates], Eindhoven (1993)

16. L. Svarovsky, Solid-Liquid Separation 4th ed., Oxford (2000)

17. A. Rushton, Solid-Liquid Filtration and Separation Technology, Weinheim (2000)

18. J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 5th ed., McGraw-Hill, USA, 1996

19. B.E. Poling, J.M. Prausnitz, J.P.O'Connell, The properties of gases and liquids, 5th ed., McGraw-Hill, USA, 2000

20. R.C. Reid, J.M. Prausnitz, B.E. Poling, The properties of gases and liquids, 4th ed., McGraw-Hill, USA, 1987

21. D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 76th ed., CRC Press, H.P.R. Frederikse, 1995-1996

22. D.W. Green (Ed.), Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill, New York, USA, 1999

23. Chemiekaarten, Gegevens voor veilig werken met chemicalien, 18th ed., TNO Arbeid, VNCI, Ten Hagen Stam, Holland, 2002

24. J. Gmehling, U. Onken, Vapor-liquid equilibrium data collection, Aqueous-Organic Systems, DECHEMA, Vol. I, part 1, Germany, 1977

25. G. Stephanopoulos, Chemical Process Control, An introduction to Theory and Practice, Prentice Hall,USA, 1984

26. Th. W. de Loos, H.J. van der Kooi, Toegepaste thermodynamica en fasenleer, Collegedictaat ST 4661, Toegepaste Thermodynamica en Fasenleer, TU Delft, 2002

27. H.J. Pasman, S.M. Lemkowitz, Chemical Risk Managment, Safety, Health, Environmental and Sustainability Aspects of Chemical Products and Processes, TU Delft, 2002

28. J.J. Heijnen, Collegedictaat biotechnologie, maart 2001

29. Dow's Fire & Explosion Index Hazard Classification Guide, 5th ed. American Intistute of Chemical Engineers, New York (1981)

30. J. Grievink, e.a., Instruction Manual Process Design, version C, PSE, TU Delft, July 2002

31. D.H. Grunwald, Syllabus Process Conditions for using Creativity in Design Work, Amsterdam, 1997

32. D.H. Grunwald, Syllabus Group Processes and Creative Methods, Amsterdam, January 2002

33. R.J. Young, P.A. Lovell, Introduction to Polymers, 2nd edition, Stanley Thornes (pubishers) Ltd, 1991

*Journals*

34. L. Jiménez, Use of butanol-water mixtures for making wheat straw pulp, Wood Science and Technology 33: 97 – 109 (1999)

35. G. Garrote, Non-isothermal autohydrolysis of eucalyptus wood, Wood Science and Technology 36: 111 – 123 (2002)

36. Y. Hong, Reactive extraction of lactic acid with mixed tertiary amine extractants, Biotechnology Techniques 13: 915–918 (1999)

37. G. Raya-Tonetti, Fluidized bed ion exchange for improving purification of lactic acid from fermentation, Biotechnology Techniques 13: 201–205 (1999)

38. M. Järvinen, Separation of lactic acid from fermented broth by reactive extraction, Bioseparation 9: 163–166 (2000)

39. A.V. Sosa, Modeling of direct recovery of lactic acid from whole broths by ion exchange adsorption, Bioseparation 9: 283–289 (2001)

40. J. Quesada, Lignin Organosolvolysis from Autohydrolyzed Corn ( Zea mays) Stalks: Ozonation of both Solvolytic Solid and Juice, Journal of Applied Polymer Science, Vol. 68, 1867–1876 (1998)

41. C. Fellers, Edgewise compression properties, A comparison of handsheets made from pulps of various yields, TAPPI Vol. 63, No. 6 June (1980)

42. J. Botello, Preliminary study on products distribution in alcohol pulping of *Eucalyptus globulus*, Journal of Chemical Technology and Biotechnology 74:141-148 (1999)

43. R. Wartena, Recycling kraft pulping chemicals: cyclic voltammetry of molten salt mixtures containing $Na_2CO_3$, $Na_2SO_4$, $Na_2S/Na_2S_x$ and $Na_2O/Na_2O_2$, Journal of Applied Electrochemistry 32: 725–733 (2002)

44. R. Wartena, Recycling wood pulping chemicals by molten salt electrolysis: cyclic voltammetry of mixtures containing $Na_2CO_3$ and $Na_2SO_4$, Journal of Applied Electrochemistry 32: 415–424, (2002)

45. D.R. Morris, Comparative Analysis of the consumption of energy of two wood pulping processes, Energy Conversion & Management 41:1557 – 1568 (2000)

46. Y. K. Hong, Reactive extraction of lactic acid with mixed tertiary amine extractants, Biotechnology Techniques 13: 915–918 (1999)

47. D. Garlotta, A Literature Review of Poly(Lactic Acid), Journal of Polymers and the Environment, Vol. 9, No. 2 (2001)

48. A.L. Woiciechowski, Experimental design to enhance the production of L-(+)-lactic acid from steam-exploded wood hydrolysate using *Rhizopus oryzae* in a mixed-acid fermentation, Process Biochemistry 34: 949-955 (1999)

49. F.D. Doyle, Reaction profile control of the continuous pulp digester, Chemical Engineering Science 54: 2679 – 2688 (1999)

50. N.C.P. Fernandes, Steady-state simulation of a continuous moving bed reactor in the pulp and paper industry, Chemical Engineering Science 55: 3729 – 3738 (2000)

51. H. Kirci, Production of dissolving grade pulp from poplar wood by ethanol-water process, Turkish Journal of Agriculture and Forestry 26: 239 – 245 (2002)

52. M. Oliet, Solvent effects in autocatalyzed alcohol–water pulping: comparative study between ethanol and methanol as delignifying agents, Chemical Engineering Journal 87: 157 –162 (2002)

53. M. Oliet, Organosolv delignification of *Eucalyptus globulus*: kinetic study of autocatalyzed ethanol pulping, Industrial and Engineering Chemistry Research 39: 34 – 39 (2000)

54. F.A. Michelsen, A comprehensive mathematic model of a continuous Kamyr digester, Applied Mathematical Modeling, Vol. 20 July (1996)

55. M.A. Gilarranz, Kinetics of *Eucalyptus globulus* delignification in a methanol-water medium, Industrial and Engineering Chemistry Research 38: 3324 – 3332 (1999)

56. J. Funkquist, Grey-box identification of a continuous digester – a distributed parameter process, Control Engineering Practice, Vol. 5, no.7 919 – 930 (1997)

57. V. Masura, A mathematical model of kraft pulping related to the alkali concentration in the cooking liquor, Wood Science and Technology 33: 381 – 389 (1999)

58. C. Martin, Ethanol production from enzymatic hydrolysates of sugarcane bagasse using recombinant xylose-utilising *Saccharomyces cerevisiae*, Enzyme and Microbial Technology 31: 274 – 282 (2002)

59. G. Kiely, Physical and mathematical modelling of anaerobic digestion of anorganic wastes, Water research Vol.31 no.3 534 – 540 (1997)

60. H. Yu, Comparative performance of mesophilic and thermophilic acidogenic upflow reactors, Process Biochemistry 38: 447 – 454 (2002)

61. H. Bouallagui, Mesophilic biogas production from fruit and vegetable waste in a tubular digester, Bioresource Technology 86: 85 – 89 (2003)

62. T.K. Bhat, Microbial degradation of tannins – A current perspective, Biodegradation 9**:** 343–357 (1998)

63. A.A. Odenyo, Tannin-tolerant ruminal bacteria from East African ruminants, Canadian Journal of Microbiology, 44: 905–909 (1998)

64. N. Rozès, Effects of phenolic compounds on the growth and the fatty acid composition of *Lactobacillus plantarum*, Applied Microbiology and Biotechnology 49: 108 – 111 (1998)

65. G. Garotte, Hydrothermal processing of lignocellulosic materials, Holz als Roh- und Werkstoff 57: 191 – 202 (1999)

66. T. Josefsson, Changes in cellulose supramolecular structure and molecular weight distribution during steam explosion of aspen wood, Cellulose 00: 1–8 (2002)

67. K. Shimizu, Integrated process for total utilization of wood components by steam-explosion, Biomass and Bioenergy Vol. 14, No. 3, 195 – 203 (1998)

68. R. San Martin, Simultaneous production of ethanol and kraft pulp from pine (*Pinus radiata*) using steam explosion, Bioresource Technology 53: 217 – 223 (1995)

69. R. Baronas, Modelling of moisture movement in wood during outdoor storage, Nonlinear Analysis: Modelling and Control, Vol.6 No.2, 3-14 (2001)

70. E. Cheshire, e.a., Kraft pulp from plantation grown biomass willow, Empire State Paper Research Institute, New York, USA (1999)

71. F.W. Lichtenthaler, Unsaturated O- and N-Heterocycles from carbohydrate feedstocks, Acc. Chem. Res., 9.9 (2001)

72. J. Gravitis, e.a., Chemicals and biofuels from hardwoods, fuel crops and agricultural wastes, Congress on energy, environment and techn. Innovation, Tokyo (2000)

73. J. Lunt, Polylactic acid polymers from corn, Cargill Dow Polymers (1999)

74. F.J. Doyle, Reaction profile control of the continuous pulp digester, Chem. Eng. Sci., 54, 2679-2688 (1999)

75. J.D. Brooker, Mechanisms of tannin resistance and detoxification in the Rumen, J. of agriculture and food chemistry, 32, 127-132 (1995)

76. T. Friesen, Pressure Screen System simulation for optimal fractionation, Paptac 88$^{th}$ annual meeting, TAPPI (2001)

77. Ü. Can, Simulation and experimental analysis of operational failures in a distillation column, Separation and purification technology 29, 163-170 (2002)

78. J. Bendzala, B.V. Kokta, *Wood Sci. Technology* 29:467, 1995

79. Chemical Market Reporter, november 2002

*Patents*

80. V.B. Diebold, e.a. (CP Associates Limited), Solvent pulping process, US 4.100.016, 17-9-1976, 11-7-1978

81. E.L.Springer (Forest Service USA), Method for selectively delignifying lignocellulosic materials, WO 99/63149A1, 2-6-1998, 27-5-1999

82. R.C. Agar, e.a., Method of recovering furfural from organic pulping liquor, US 5.788.812, 7-6-1995, 4-8-1998

83. J.S. Shabtai, e.a. (University of Utah Research Foundation), Process for conversion of lignin to reformulated hydrocarbon gasoline, US 5.959.167, 19-8-1998, 28-9-1999

84. E. Rousu, e.a. (Kolster OY AB), Method for producing furfural, acetic acid and formic acid from spent pulp-cooking liquor, WO 02/053829A1, 29-12-2000, 11-7-2002

85. R.L Farrell (Jacobson, Price, Holman and Stern Professional Limited Liability Company), Fungi for improvements of wood and pulp appearance and qualities, US 2.002.096.273, 30-3-2001, 25-7-2002

86. R.C. Wingerson (Purevision Technology Inc.), Method of treating lignocellulosic biomass to produce cellulose, US 6.418.788, 16-8-2000, 16-7-2002

87. R. Katzen, J.H. Lora, e.a. (Repap Technologies Inc.), Recovery of lignin, US 4.764.596, 11-12-1986, 16-8-1988

88. J.H. Lora, R. Katzen, e.a. (Repap Technologies Inc.), Pulping of fibrous plant materials and recovery of resultant by-products, WO 9315261, 29-1-1992, 5-8-1993

89. R. Leblanc, e.a. (Repap Technologies Inc.), Pulping of lignocellulosic materials and recovery of resultant by-products, WO 9213849, 1-2-1991, 20-8-1992

90. T.N. Kleinert, Organosolv pulping and recovery process, US 3,585,104 (1971), 15-6-1971

91. Chang et al, Pulping of lignocellulose with aqueous alcohol and alkaline earth metal catalyst, US 4594130 (1986), 10-6-1986

*Theses*

92. R.P. Affleck, Recovery of xylitol from fermentation of model hemicellulose hydrolysates using membrane technology, Virginia Polytechnic Institute and State University (2000)

93. Z. Chen, Primary Driving Force in Wood Vacuum Drying, Virginia Polytechnic Institute and State University (1997)

94. Z. Szengyel, Ethanol from wood, cellulase enzyme production, Department of Chemical Engineering 1, Lund University, Sweden (2000)

95. E. Muurinen, Organosolv pulping – a review and distillation study related to peroxyacid pulping, Department of Process Engineering, University of Oulu, Finland (2000)

96. J. Buhner, Dilute acid hydrolysis and fermentation of corn fiber to xylitol, Department of biological systems engineering, Virginia Polytechnic Institute and State University, USA (2000)

97. W. Olek, The inverse method for diffusion coefficient identification during water sorption in wood, Department of agricultural engineering, Agricultural university of Poznan, Poland (2000)

98. Ari Ämmälä, Fractionation of thermomechanical pulp in pressure screening, Department of process and environmental engineering, University of Oulu, Finland (2001)

*Sites*

99. http://www.sssdynamics.com/scrstrat.html

100. http://www.steamexplosion.com/

101. www.paperinfo.fi

102. http://www.wateremissies.nl/documenten/steunpunt/RIZA96027.pdf

103. http://www.matche.com/EquipCost/Index.htm

104. http://www.unece.org/trade/timber/docs/tc-60/presentations/6-1-prins.ppt

105. http://www.ecn.nl/phyllis

106. http://www.groen.net/magazine/artikel.cfm?PG=1&arts=535

107. http://www.den.novem.nl/den2002.htm

108. http://www.nen.nl/

109. http://www.nen.nl/nl/pro/normshop/

110. http://www.vt-vsa.org/wood.html

111. http://www.expsep.co.uk/SWE.html

112. http://www.fcq.uach.mx/licenciaturas/temarios/unitarias I/tema5.pdf

113. http://www.om.com/pulpex/statistics/stats.asp

114. http://www.coprinox.it/dryers.htm

115. http://fourier.che.udel.edu/publications/PDF/doy99a.pdf

116. http://www.cheresources.com/ctowerszz.shtml

117. http://www.omnivent.nl/nl/luchtcalc.html

118. http://www.water-wastewater-treatment.com/screwpress.html

119. http://members.rogers.com/fhcurry/CEIRev3.xls

120. http://europa.eu.int/comm/food/fs/sc/scf/out96_en.pdf

121. http://www.cheric.org/kdb/kdb/hcprop/cmpsrch.php

122. http://www.sdcattlemen.org/Value/Where's%20the%20Feed.htm

123. http://www.portalenergy.com/caddet/eetb_eut/R151.pdf

124. http://www.apo.nmsu.edu/Telescopes/SDSS/eng.papers/19950926_-ConversionFactors/19950926_MProperties.html

*Consulted firms*

125. Norske Skog Parenco B.V.
(http://www.norske-skog-na.com/team/europe.xml - Parenco)
Contact with Mr. B. Kortekaas

126. Stake technology Ltd. (http://www.staketech.com/)
Contact with Mr. J.D. Taylor

127. SHR hout research (http://www.shr.nl/)
Contact with Mr. B. Tjeerdsma

128. FKC Screwpress Co., Ltd. USA (www.fkcscrewpress.com)
Contact with Mr. J. Capell

129. Vincent Corporation, Florida, USA (www.vincentcorp.com)
Contact with Mr. G. Mewhinney

130. Maruishi Co., Ltd. Shizuoka, Japan (www.maruishi.com)

131. Hans Huber AG, Berching, Germany (www.huber.de)
Contact with Mr. O. Christ

132. Andritz, AG, Gratz, Austria (www.andritz.com)
Contact with Mr. R. Puhr

133. Paques (http://www.paques.nl/)
Contact with Mr. R. Mulder

*Consulted persons from Delft University of technology*

134. Prof.dr. R.A. Sheldon (Biocatalysis and Organic Chemistry)

135. Ir. M. Behrens (Apparaten voor Proces Industrie)

136. Dr.ir. J.A. Jongejan (Enzymology)

137. Prof. Dr. Ir. J.J. Heijnen (Bioprocess technology)

138. Jan Marijnissen (universitair hoofddocent Particle Technology)

139. dr. K. Janssen (Organic Chemistry and Catalysis)

140. ing. M. Valentijn (Process Systems Engineering)

141. ir. H.H. Kleizen (Particle Technology)