CPD NR 3309
Conceptual Process Design

Process Systems Engineering
DelftChemTech - Faculty of Applied Sciences
Delft University of Technology

Basis of Design:
Design of a life-cycle chain from biomass acquisition and transport to the production of Synthesis Gas for Shell Middle Distillate Products through large-scale gasification of biomass in the Rotterdam Harbour area

Authors	*(Study nr.)*	*Telephone*
M.E. Djatmiko	1059300	06-24578184
W. Hensen	1046624	06-10067854
E.M. Herben	9328149	06-21828025
A. Kurniawan	9489256	06-22923838
B.J. Vreugdenhil	1113712	015-2140201

Keywords
Syngas, sustainability tool, gasification, biomass, wood, life cycle, Biomass to Liquid (BTL).

Assignment issued   : April 19th 2004
Report issued   : July 30th 2004
Appraisal   : August 6th 2004

Preface

This conceptual process design project is part of the Master's curriculum of the study Chemical Engineering at Delft University of Technology. After more than three months hard working during the summer days, a lot of long brainstorming sessions and hundred litres of coffee and tea, the basis of design is finally finished.

The basis of design would not have been possible without the help of the following persons: M. Kanaar and O. Rens from the NUON Power Plant in Buggenum, C. Daey Ouwens from Eindhoven University of Technology, H. Boerrigter from ECN, A. Faaij from University of Utrecht, H. Harmsen from KPMG Netherlands, J.R. Arcate from Transnational Technology in Honolulu (Hawaii), M. Valentijn and A. van Geffen from Delft University of Technology, J. van den Berg from Vliegasunie, Carolien, Dirk and Richard from the environmental discussion group and all the survey participants. Moreover we would like to thank our family and friends, who supported us during this project.

Delft, July 30th 2004

CPD 3309
Andy Kurniawan
Berend Vreugdenhil
Emile Herben
Lissa Djatmiko
Wilma Hensen

TUDelft

Summary

It is the intention of the European Commission to replace a substantial amount of the European transport fuel market by biofuels, starting from 2005. A promising way to produce biofuels is to produce high quality diesel from biomass via gasification, followed by a Fischer Tropsch process. Fischer Tropsch diesel can replace conventional diesel without requiring engine modifications. This design study looks at the large-scale production of synthesis gas from biomass through gasification, as feedstock for the Fischer Tropsch process. Not only the gasification plant has been designed; the logistics has also been investigated.

The focus in this design has been on sustainability. Two different tools for measuring sustainability have been used and the final process is a result of the tools' recommendations. The designed plant will be situated in the Rotterdam Harbour area. Because of the scale of the process, biomass needs to be acquired from overseas. Several different biomasses and pre-treatment options have been investigated, as well as various process chain options. This has resulted in a relatively sustainable design, producing little waste, and with a thermal efficiency of 87 %. It uses wood residues from the Baltic States and Sweden. Pre-treatment in the form of chipping an pelletising of the wood takes place overseas, resulting in a large reduction of transportation costs. Gasification takes place at elevated pressure with oxygen in a circulating fluidised bed gasifier. The resulting product gas is further cracked to syngas in a tar cracker and then desulphurized in a high temperature cleaning section using sorbent. Membranes are used to separate the carbon dioxide from the syngas before it is sent to the FT process.

The plant has a production capacity of 30,000 ton syngas per day and needs a feedstock of some 65,000 ton wood per day.

The plant's capacity is estimated to be 1-2% of the European fuel market in 2020. Commercial biomass gasification plants do not yet exist. The same holds for large-scale biomass gasifiers. A significant increase in thermal input of gasifiers is required for the use in such large-scale applications.

The designed supply chain requires a very large investment. Unless a set of major changes takes place, like e.g. a decrease in major equipment costs, an increase of the syngas price or income through CO_2 sequestration, this process will not be economically viable. The high equipment costs pose as the biggest financial problem.

The economic evaluation is based on a syngas price of 5.4 €/GJ and a yearly production of 8000 hours. This is a refinery standard, which requires 91% uptime. The plant is designed to run for 20 years.

Other risk factors for the design are the large dependence on a single feed source, which has to be transported over a large distance before being converted into syngas, and the high required uptime.

The design could be improved with a more extensive use of heat integration. The development of gasification kinetic models is desired for better equipment design.

TUDelft

Table of Content

TUDelft

TUDelft

TUDelft

TUDelft

1. Introduction

Since the last decade the interest in renewable energy is growing as a result of the increasing concern about global warming and the resulting climate change. The European Commission decided to accelerate the reduction of oil dependency and CO_2 emission using the recently introduced biofuel directive. This directive demands that the member states a share of 2% in 2005 and 5.75% in 2010 of the fossil fuels sold on their transportation markets be replaced by biofuels (fuels made from biomass) [1]. An important advantage of biofuels is that the emission of the greenhouse gas CO_2 can be diminished when renewable transportation fuels are used. Biomass will close the life cycle chain of CO_2. Growing biomass consumes CO_2 from the atmosphere. CO_2 is released back into the atmosphere when biomass is converted to fuels and burned. Hence, the total amount of CO_2 in the atmosphere remains constant, which is not the case with fossil fuels. The CO_2 emission level could even become lower when CO_2 is sequestrated in one of various methods, such as CO_2 storage in the oil reservoir.

Biodiesel from oil crops and ethanol from sugar beets are already commercialised in several countries, for example Brazil. However these traditional biofuels have disadvantages in land use, costs and potential to reduce CO_2 emissions. Sugar cane ethanol and advanced biofuels that are produced from woody biomass via gasification or via fermentation have much better perspectives [2]. One of those promising future biofuels is Fischer-Tropsch diesel; this is produced by a combination of biomass gasification (BG) and Fischer-Tropsch (FT) synthesis. The biomass is partially oxidised to syngas, and this syngas is converted via the FT process into clean liquid fuels (e.g. diesel). Other than converting to FT fuels, syngas is used to produce bulk chemicals, such as ammonia, methanol, hydrocracking and hydrogenation products.

The subject of this Conceptual Process Design (CPD) as given in the project description is:

> *Design of a life-cycle chain from biomass acquisition and transport to the production of Synthesis Gas for Shell Middle Distillate Products through large-scale gasification of biomass in the Rotterdam Harbour area.*

The main objective of this CPD project is to design a logistics chain for the supply of biomass to Rotterdam and a chemical plant to produce synthesis gas (or syngas, a mixture of CO and H_2) with a H_2/CO ratio of 2 and a pressure of 40 bara at 500 K. The amount of syngas produced is equivalent to a LHV of 8000 MW, which serves totally as input for the Shell Middle Distillate Synthesis (SMDS) plant.

The diesel produced with the FT process has to face tough competition from the cheap fossil fuels, but also from biodiesel from fermentation, bioethanol and biomethanol. In Brazil, bioethanol is already produced in large scale for transportation fuels. Current selling price of fossil diesel fuel is 0.87 €/litre, of which almost 70% are taxes [3], so the production cost will be 0.27 €/litre. Biofuels cannot yet be produced against such low prices. Biodiesel from rapeseed and soybeans will have an average price of 0.56 €/litre, respectively 0.76 €/litre, according to recent studies [4]. The use of syngas for the

production of FT-diesel will give a diesel price of 0.44 €/litre [5]. To make FT-diesel competitive with fossil fuel derived products, a tax exemption and a significant increasing in oil prices will be required. However, FT-diesel has the advantage of being a very clean liquid in comparison with the current diesel sold; it contains almost no sulphur or aromatics.
Local conversion of natural gas into shippable hydrocarbon liquids by FT is demonstrated on full commercial scale by Shell in Malaysia. Also SASOL in South Africa applies FT synthesis on commercial scale to produce diesel from coal. However, no commercial process for the production of FT-diesel from biomass does yet exist [2].

This plant will have an enormous impact. The 8000 MW of syngas it produces is 16% of the world capacity of syngas in 2004, 50 GW_{th} [1]. It will produce 1-2% of the European fuel market in 2020 [7]. Just it its sheer size, not only in Rotterdam, as well as in the biomass producing countries will ensure a great impact on national economy, society and environment. That is at the same time the big challenge of the design; (very) large-scale gasifiers do not yet exist, as well as a large-scale reliable hot gas cleaning [8]. A challenge will also be the guaranteed supply of biomass feedstock.

The principals of this CPD project are J.W. Coppelmans and T.J. Faber, who are doing their Master Graduation Thesis for Chemical Engineering on designing sustainability tools ([9][10]). They are interested to test their sustainability tools in this Conceptual Process Design project, to see whether a sustainable process design can be obtained by using these tools. Moreover, they want to have feedbacks on their tools. In this design, focus has been on the tools as they were used when making critical design selections.
Additionally, Shell wants to investigate indirectly whether biomass can be used to produce syngas for their possibly-to-be-built SMDS plant (2015) in Rotterdam Harbour area.

The sustainability tool created by T.J. Faber, called CPD-SAT, is aimed used in the early stages of the CPD. It is used to select the most sustainable biomass and logistics chain.
The other tool, created by J.W. Coppelmans, called SUSDAT, is used to obtain one sustainable chain of unit operations from biomass to syngas by comparing different chains (block schemes) of unit operations on specific chosen sustainability indicators.

Several issues are listed below, which are or not done during this CPD project.

Issues, which will be done:
- Delft Design Matrix [10], as working method is pursued as far as possible.
- AAA (Advanced Activity Assistant) is used for activity planning.
- The process and option selection is considered as the main focus of this CPD project based on the sustainability by applying the two sustainability tools: CPD-SAT and SUSDAT.
- Brief investigation of different feedstock in early phase of project is performed using literature search and survey on the stakeholders' opinion.

- Other than the process, the whole supply is regarded as the design project, where the logistics chain is investigated.
- The software system GaBi 4 is used to create life cycle balances LCA, which can be used in the sustainability tools. Other balances like SLCA and LCC are calculated using some literature data or assumptions.
- During this CPD project, decisions are based on the outcome of two sustainability tools.
- Development of the sustainability tools since those two are not ready to use when they must be applied. A lot of updates and data are provided for those tools.
- The winning case for the process selection is compared with current practice, the Shell Gasification Process, a part of the SMDS process.
- Another survey is carried out to identify what the stakeholders consider as the most important issues and indicators in building a chemical plant.
- A discussion with environmental group is performed to get more feedbacks on the design, where some important environmental issues can be taken into account in the designing of the project.
- The social aspect of the process is investigated by short interviews and discussion.
- Simulation of the biomass gasification process in the flow sheet modelling tool ASPEN PLUS.
- Stimulation of the creativity using the BAWEL Creativity Tool.
- A plant visit to a coal power plant in Buggenum is organized in order to get real picture of a similar process.
- Belbin group roles are evaluated three times during the project, at the beginning of the project, after pre-BOD and at the end of the project.

Issues, which will be not be done:
- Changing production site of biomass gasification. Although it also seems very attractive to build the plant nearby the feedstock source location, the biomass gasification will only be done in Maasvlakte, Rotterdam Harbour area as described in the project description.
- Equipment design is not considered as the main focus of the whole project.
- The gasification reactor is not modelled with kinetic, since the kinetic data is still unknown and it is very difficult to define the biomass in ASPEN PLUS. Therefore a conversion data from literature is used to set up the mass balance.

TUDelft

2. Process Options and Selection

In this chapter a short explanation is given on the gasification process and the mode of operation. Thereafter a brief description is given of the results of the two sustainability tools. CDP-SAT is used to select the most sustainable feedstock options, whereas SUSDAT is used to select the most sustainable chain of unit operations (or tasks). In Chapter 5 more details of the gasification process and the chosen unit operations will be given and discussed.

2.1. The biomass gasification process

Gasification is defined as the act or process of converting into gas [12]. Biomass is defined as plant materials and animal waste used as fuel or as the total mass of living matter in a given unit area [13]. Gasification of biomass is thus the process that converts plant materials or animal waste into gas. In this process syngas for the Shell Middle Distillate Process should be produced. Gasification to syngas comprises two main reactions:

$$C_nH_m + n/2 \; H_2O \rightarrow n \; CO + (m/2+n/4) \; H_2 \qquad\qquad (2.1)$$

$$C_nH_m + n/2 \; O_2 \rightarrow n \; CO + m/2 \; H_2 \qquad\qquad (2.2)$$
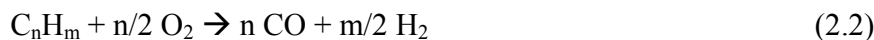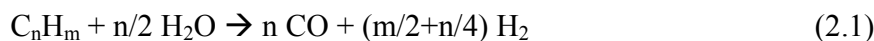
Reaction 2.1 is the actual gasification reaction that is endothermic. To make the process autothermal, the exothermic reaction 2.2, should take place to provide the heat needed for reaction 2.1.

These reactions should take place on large-scale to produce 8000 MW of syngas. The word 'large-scale' into the project description almost immediately tells that the biomass gasification process should be operated continuously. This is also encouraged by the guidelines J.M. Douglas [14] provides about batch versus continuous processes.

2.2. Selection of supply chain using CPD-SAT

2.2.1. Problem definition

In this section the CPD-SAT tool of T.J. Faber [10] is used to assess the differences in sustainability behaviour of supply chain alternatives for the supply of syngas (CO/H_2) in Rotterdam with the specifications given in Table 3.1 in Chapter 3. This Life Cycle Assessment is carried out in order to support the decision for selecting the most sustainable feedstock for syngas production. The supply chain is here defined as the chain of logistics and the actual chemical process in Rotterdam. In Figure 2.1 the supply chain and its boundaries are graphically presented.

TUDelft
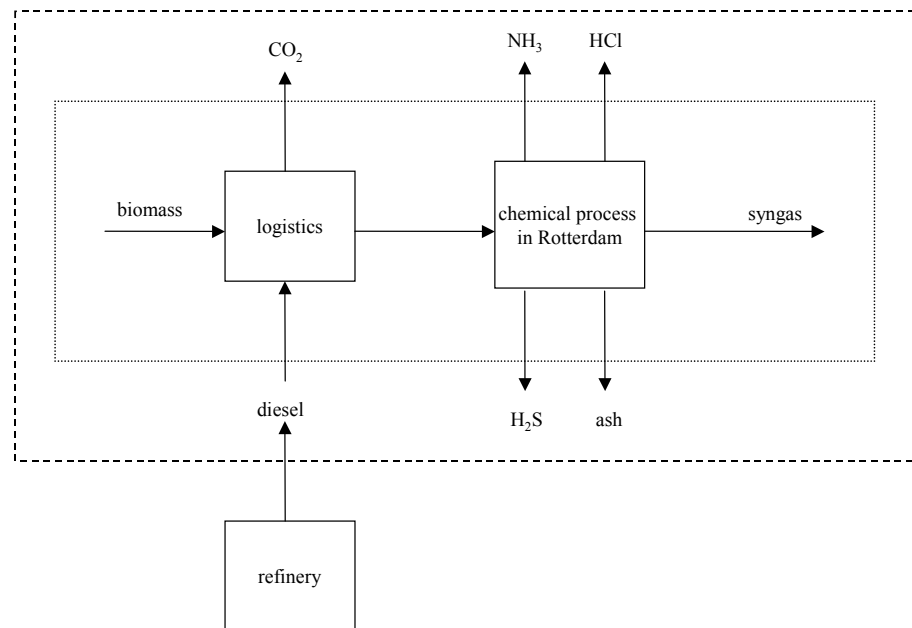
product-environment boundary ·····················

cut off boundary - - - - - - = product system boundary

Figure 2.1: Supply chain of the process as used for CPD-SAT

Some important assumptions in this stage of the design:

- Unlike the system boundary used further ahead in the design, diesel, used for transportation of biomass and the emissions caused by transportation are also taken into account in CPD-SAT for the purpose of LCA calculation.
- The production of diesel for transportation is not taken into account.
- Transport of biomass takes place in the land of origin with trucks to the nearest harbour and on sea with large ships to Rotterdam.
- All impurities, which are coming out of the process in Rotterdam, are unloaded in the environment as NH_3, H_2S, HCl and ash (waste).
- Waste treatment is not taken into account, i.e. the system ends where the impurities are unloaded in the environment.
- The energy efficiency of the chemical process in Rotterdam is assumed to be 65% (based on LHV).

The CPD-SAT tool uses indicators, or so-called impact categories, to measure the sustainability of a process. These impact categories try to cover all the parameters that define sustainability. The more sustainable a process is, the higher its scores are for the indicators. An overview of the applied impact categories can be found in Appendix 2.1.

2.2.2. Synthesis and definition of the cases

Different feedstock alternatives are generated by brainstorming sessions. Details can be found in Appendix 2.2. After quick selection, five possible feedstocks, listed in Table 2.1, are further investigated with the tool. The feedstock alternatives are further explained in Appendix 2.3.

Table 2.1: Supply chain alternatives

Option	Feedstock	Land of origin
1.	Wood residues	Baltic States, Finland and Sweden
2.	Energy crops	Brazil
3.	Fresh wood	Baltic States
4.	Agricultural waste	West Europe
5.	Manure	United States

A software program, called 'GaBi' (Ganzheitlichen Bilanzierung) is used to calculate a large part of the Life Cycle Indicators. As an example the GaBi model for manure is given in Figure 2.2.

Manure from America

GaBi 4 process plan: Mass
The names of the basic processes are shown.
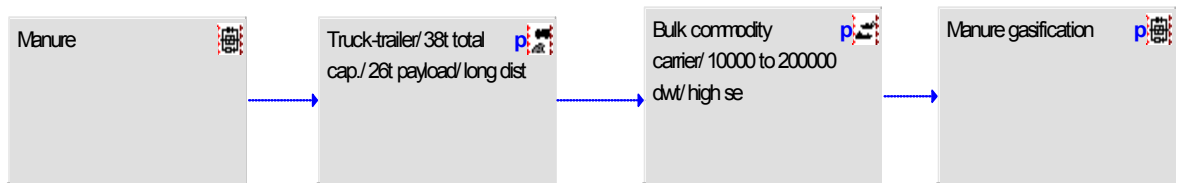
Figure 2.2: Typical model in GaBi

2.2.3. Analysis of the cases
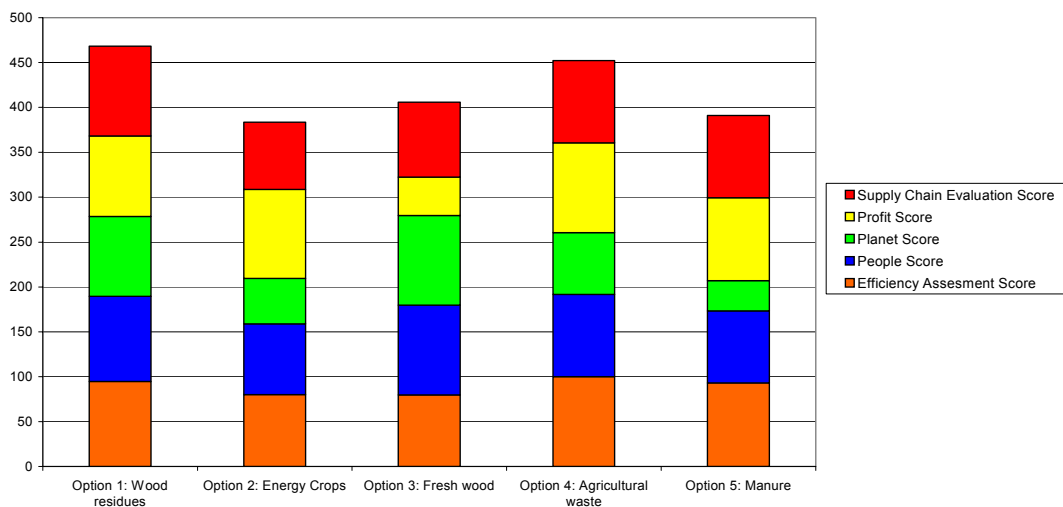
Figure 2.3: Overall ranking from the CPD-SAT tool of the different supply chain alternatives

The overall ranking of the supply chain alternatives from the CPD-SAT tool is shown in Figure 2.3. The best option on sustainability is the option with the highest score. The tool indicates wood residues as the overall most sustainable option. All graphical representations of the different categories scores for Efficiency Assessment, Triple P and Supply Chain Evaluation can be found in Appendix 2.4. The table with the scores of the five options for all the impact categories can be found in Appendix 2.5. The reasoning behind the quantitative and qualitative scores and their data sources is also given in Appendices 2.5. Since Social Life Cycle Assessment is applied in the CPD-SAT tool, social acceptance of the chosen feedstock is very important. The social acceptance is investigated by survey on the opinion of the stakeholders. The results of this survey are taken into account the application of CPD-SAT tool and these can be found in Appendix 2.6.

2.2.4. Winning case

As already stated, the option wood residues from the Baltic States and Scandinavia are the most sustainable option according to CPD-SAT. In Figure 2.3 it can be seen that wood residues scores on all categories almost the maximum score (100). It is likely that the tool selects wood residues as the most sustainable option because:

- Fresh wood should be eliminated because the economic margin is negative.
- Manure scores lower on planet, because a lot of impurities are present in the manure, mainly the sulphur content and because of the large distance between the land of origin and Rotterdam.
- Energy crops scores lower on planet and supply chain evaluation, because of the large distance from Rotterdam and the social acceptance for energy crops is very low.
- Agricultural waste is also a sustainable option according to the tool, but rejected because collection and the competition with other uses of this waste can become a problem. Nowadays agricultural waste is left on the farmland for fertilizer or used as animal food.

Wood residues come from different sectors, mainly from forestry and industrial sawmills. This waste cannot be used anymore for production of woody materials and can therefore be burned or converted. Wood residues consist of the tops and branches of trees that are left after harvesting when the round wood has been removed for lumber or producing pulp and paper.

2.2.5. Evaluation

Table 2.2: Important issues to consider for wood residues

Hot spot	Caused by design variables:
Emission costs	Composition and amount of biomass
Feedstock costs	LHV of biomass, the price, amount of biomass
Eutrophication	Distance from Rotterdam and density of biomass for transport
Acidification	Distance from Rotterdam and density of biomass for transport
Material intensity	LHV of biomass and energy efficiency of process

TUDelft

The option of wood residues does not really have any serious "hot spots"; as mentioned above, it scores on all categories high. However, points with relatively lower scores and their causes are given in Table 2.2.

All these "design variables" are, in fact, (to a large extent) fixed values. For example, one cannot change the properties of wood. The things one might be able to change are:

- the distance from Rotterdam, but it is not likely to find large amounts of wood residues close to Rotterdam
- the density of biomass, through pre-treatment of the wood residues, thereby decreasing the amount for transportation
- the amount of biomass needed, by designing a more energy efficient process.

2.3. Selection of chain of unit operations using SUSDAT

2.3.1. Problem definition

In this section the SUSDAT tool of J.W. Coppelmans [9] is used to obtain one sustainable chain of unit operations from biomass to syngas by comparing different chains (block schemes) of unit operations on specific chosen Key Sustainability Indicators. For further details about the SUSDAT tool, a complete explanation can be found in the graduation thesis of J.W. Coppelmans [9].

The KSI are chosen from an extensive list of indicators, given by SUSDAT and based on the triple bottom line (People, Planet and Profit), as shown in Appendix 2.7. When choosing KSI, it is expected that these indicators will show large differences in the scoring for the different cases, thereby making it easier to see differences in sustainability between the cases. In Table 2.3 the KSI are given with the motivation why these indicators are chosen. The choices are also supported by the results of the questionnaire on the stakeholders' opinion (Appendix 2.8).

Table 2.3: Key Sustainability Indicators (KSI)

Key Sustainability Indicator	Motivation
New Technology (People)	Each development of technology can mean a better process then the current practise, which among other things also can give more social benefits like creating more jobs in R&D, or reducing the noise level.
Sustainable feedstock (People)	Since the input of biomass is large, it could be difficult to grow enough biomass to have a sustainable feedstock. Reactor type and conditions greatly determine the amount of biomass used.
Global Warming potential (Planet)	A lot of carbon dioxide is produced. Global warming potential is nowadays a hot topic. Also encouraged by questionnaire results.
Human Toxicity Potential (Planet)	Human health is a valuable good. Also encouraged by questionnaire results.
Return on Investment (Profit)	One of the most important issues in economic analysis, which is often used to compare processes in the design phase.

TUDelft

A benchmark process is defined to compare all indicators (KSI as well as non-KSI) in the triple bottom line (People, Planet and Profit) with the most sustainable block scheme of unit operations. For this comparison, the current practice, that resembles the biomass gasification process the most, is chosen. The chosen benchmark process is the Shell gasification process (SGP), which is part of the Shell Middle Distillate Synthesis (SMDS) process. SMDS is a process for the polymerisation of natural gas into liquefied products ranging from transportation fuels to lubricating oils and waxes. It is already commercialised in Bintulu, Malaysia, which has a capacity six times smaller than the required capacity of this project.

2.3.2. Synthesis and definition of cases

The block scheme of the supply chain, used in the previous section (section 2.2) can be divided into three sections, as given in Figure 2.4. Pre-treatment can take place in the country of origin or in Rotterdam.
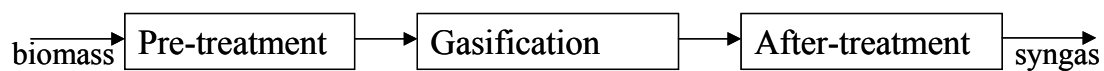
Figure 2.4: Block scheme of process divided in different sections

During the second step of SUSDAT, possible unit operations for pre-treatment, gasification and after-treatment have been generated through brainstorm sessions and literature research. The different unit operations are listed in Appendix 2.9.

For SUSDAT it is necessary to set up block schemes of different chains of unit operations. The block schemes are set up on condition that:
- The order of the chain is technically possible (Appendix 2.9, e.g. hot gas removal is always combined with high pressure operation or choice of pre-treatment in Baltic States)
- The chain should meet the specifications of the syngas
- All listed unit operations in Appendix 2.9 are covered
- The block schemes differ on various unit operations of each other.

In Table 2.4, seven different cases of block schemes are defined. The detailed description in flow sheets per case is given in Appendix 2.10.

Table 2.4: Cases and their motivations

Case	Name	Motivation
A	*CFB + EF + Cold Gas Cleaning*	• No energy-consuming milling needed. • Fast-drying using microwaves. • Less transport loading by chipping in land of origin.
B	*CFB + OLGA + Bio Claus*	• Relatively low temperature process, thus less biomass needed. • No energy-consuming milling needed.
C	*Fixed Bed + Cold Gas Cleaning + Hydrogen Mixing*	• No tar production in the entrained flow reactor. • Slag contains the minerals. • Proven technology.

TUDelft

Case	Name	Motivation
D	*Pyrolysis + EF + Cold Gas Cleaning + Hydrogen Mixing*	• Pyrolysis liquid is easier to handle than solids • Less biomass input, since hydrogen is added. • Less transport due to pyrolysis and EF for good conversion
E	*CFB + Hot Gas Cleaning*	• No energy-consuming milling needed. • High pressure, thus smaller equipment. • Less waste through the use of sorbent. • No solvents needed through the use of sorbent and membrane.
F	*CFB + Wet Gas Cleaning + Hydrogen Mixing*	• Relatively low temperature process, thus less biomass needed. • Rectisol used in this option is a superb purification device for CO_2 and H_2S removal.
G	*Torrefaction + EF + Hot Gas Cleaning*	• Less waste through the use of sorbent. • No solvents needed through the use of sorbent and a membrane. • Easy milling due to the torrefaction process

2.3.3. Analysis

The analysis of cases consists of two steps:
1. Calculating Key Sustainability Indicators
2. Optimizing the weighing of Key Sustainability Indicators
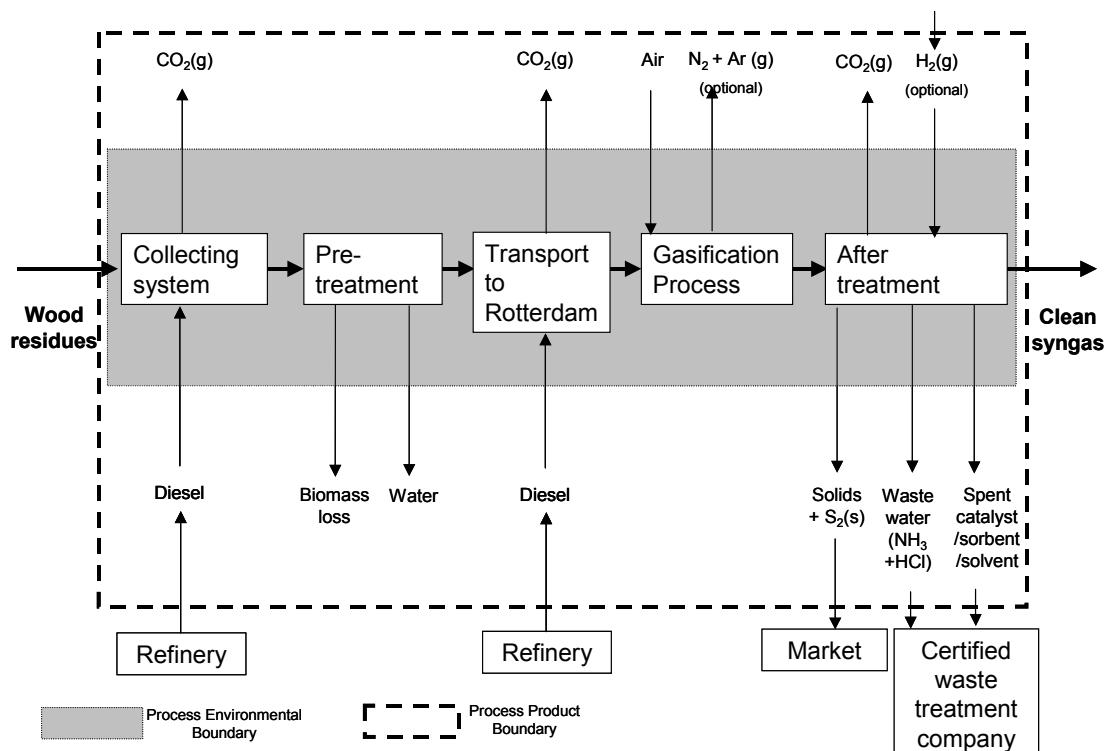
Figure 2.5: System boundaries for calculation of Key Sustainability Indicators

TUDelft

In order to calculate Key Sustainability Indicators, system boundaries as shown in Figure 2.5 are defined, where all waste treatments are performed by certified sustainable companies. Therefore, all waste streams have negative prices. For the optional hydrogen input, it is assumed to purchase from a certified sustainable refinery or other gas producer, like Air Products. The solids, like ash and dust, and sulphur are sold as by-products to market. The by-product CO_2 is discharged to the environment. No sequestration is taken into account. The nitrogen produced from the air separation plant is assumed as product. Wood residues loss and water from the pre-treatment process are discharged to the environment. Since the large amount of wood residues must be transported from the land of origin, a vessel is chosen. As fuel for the vessel diesel from certified refinery, like Shell, is used.

2.3.4. Calculating Key Sustainability Indicators

For each case, the scores for the Key Sustainability Indicators are determined by setting up overall mass balances, energy input, economic margin and investment cost of major equipments. The data and assumptions, which were used to calculate the balances and KSI (Appendix 2.10), are given in Appendix 2.11.1, 2.11.2, 2.11.3 and 2.13. In Figure 2.6 all normalised values of the KSI of each case are shown. The values of KSI of each case are given in Table 2.5.
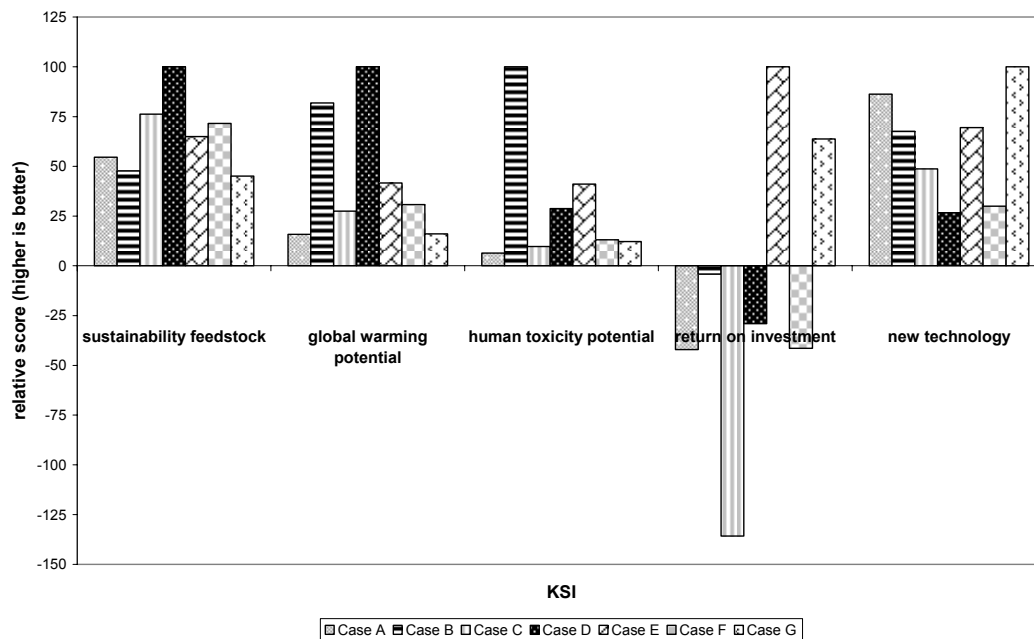
Figure 2.6: KSI scores of all cases

Table 2.5: **All values of KSI of each case**

KSI	Unit	Case A	Case B	Case C	Case D	Case E	Case F	Case G
New Technology	[€ / functional unit]	0.016	0.012	0.0088	0.0043	0.012	0.0054	0.018
Sustainability feedstock	[biomass use / functional unit]	11.0	12.7	7.9	6.0	9.3	8.4	13.4
Global Warming Potential	[kg CO2-Equiv. / functional unit]	18.0	3.5	10.4	2.9	6.9	9.3	17.8
Human Toxicity Potential	[kg DCB-Equiv. / functional unit]	0.19	0.012	0.12	0.042	0.029	0.092	0.098
Return on Investment	[%]	-8.2	-0.8	-26.5	-5.7	19.5	-8.1	12.4

2.3.5. Optimizing the weighing of Key Sustainability Indicators

SUSDAT optimises the weight factors for all KSI of each case by using Data Envelopment Analysis (DEA) [9], a quantitative technique for measuring the relative efficiency (performance) of relatively homogeneous organizational units. The cases are ranked according the outcome of the DEA.

Table 2.6 shows the results of the DEA of each case with the Average Efficiency and the Times Efficient.

Table 2.6: **Result of DEA of each case (Average Efficiency & peer group frequency)**

	Case A	Case B	Case C	Case D	Case E	Case F	Case G
Optimized for case A	100%	72%	79%	59%	100%	46%	99%
Optimized for case B	-30%	100%	-136%	-38%	85%	-39%	38%
Optimized for case C	100%	73%	80%	60%	100%	47%	97%
Optimized for case D	67%	100%	61%	71%	100%	39%	73%
Optimized for case E	18%	100%	-68%	-5%	100%	-10%	66%
Optimized for case F	100%	73%	80%	60%	100%	47%	97%
Optimized for case G	100%	72%	79%	59%	100%	46%	99%
Times efficient	4	3	0	0	6	0	0
Average	59%	86%	16%	34%	98%	22%	78%

2.3.6. Winning case

As shown in Table 2.6, it is clear that case E is the most sustainable chain of unit operations: it is up to 6 times more efficient than other cases and it has the highest average efficiency score. In Appendix 2.10, the block scheme of the winning case can be found. The winning process consists of a pre-treatment in the Baltic States, viz. chipping and pelletising of the wood residues. In Rotterdam, the pellets are gasified in a circulating fluidized bed reactor, followed by a catalytic cracker to remove tars and convert the product gas into syngas. The gas is then cleaned with Zn/Ti sorbent, which removes COS, H_2S and HCl, and a water-gas shift reactor is used to adjust the H_2/CO ratio. Finally, a membrane is used to remove the CO_2 from the gas stream.

In Table 2.7, the KSI values of the winning case with their optimal weight factors are summarized. The meaning of these KSI values and optimal weight factors is discussed shortly, as following:

- Only one of the *input* indicators, Sustainable Feedstock, has a weight factor. It means that it is taken as the most important issue.

- For the *output* indicators, it is difficult to determine which indicator has the largest influence in the weight factor. The value of New Technology is very low, and this is the reason why its weight factor becomes very high. If the KSI scores are normalized in a scale of 0-100, both indicators can be better compared.

The winning case is analysed with these optimal weight factors, which emphasize New Technology, Sustainable Feedstock and Return of Investment.

Table 2.7: KSI values of winning case and weight factors of each KSI

KSI	Unit	Desired High (1) or Low (0)	KSI scores of Case E	Weight factor of case E
New Technology	[€ / functional unit]	1 - output	0.012	3044.8
Sustainability feedstock	[biomass use / functional unit]	0 - input	9.3	10.8
Global Warming Potential	[kg CO2-Equiv. / functional unit]	0 - input	6.9	0.0
Human Toxicity Potential	[kg DCB-Equiv. / functional unit]	0 - input	0.029	0.0
Return on Investment	[%]	1 - output	19.5	3.2

2.3.7. Evaluation of sustainability of design

When the analysis of all cases by SUSDAT is finished, several sustainability issues, which determine the choice of KSI and the (un)sustainability of design, and process-choices in unit operations are evaluated.

First, it is not possible to see what are the most important factors (or unit operations) that cause a good or a bad score on the different KSI. Neither SUSDAT can point out which unit operations are the most sustainable ones, nor does a quick "manual" investigation give more explanation. Only one issue, biomass use, can be seen clearly that it will determine the sustainability of the design.

Looking at the results, using common engineering sense, case E is the most sustainable option, because of the following points:

- It uses a Circulating Fluidized Bed (CFB) reactor, instead of an Entrained Flow (EF) reactor. A CFB is operated at around 850°C, while an EF at 1400°C. This temperature difference means that an EF needs to burn more biomass in order to reach these high temperatures, thereby increasing the amount of biomass needed for 1 kg of diesel, which is one of the KSI.
- It uses sorbent for the removal of impurities from the gas stream, instead of water scrubbers, thereby reducing the amount of waste produced (water from the scrubbers is taken as waste in the models) and reducing the costs for waste treatment.
- It uses a membrane for the removal of CO_2 from the gas stream, instead of a solvent system, thereby again reducing the amount of waste produced and decreasing the health issues, otherwise caused by these solvents.

Looking at the results per indicator in Figure 2.6, there are some large differences in the scores of each case. From the "sustainability feedstock" indicator, it seems that the water-gas shift reactor is the biggest cause for an increase in biomass needed per kg of product.

This is very logical, since the water-gas shift reaction converts CO into H_2, so more CO is needed and thus more biomass is needed. The alternative for the water-gas shift reactor is the addition of hydrogen, and since this is purchased, this has no impact on the amount of biomass needed per kg of product (instead, it has a (large) negative impact on the economic margin of the process). The winning case uses a water-gas shift reactor for the conversion of CO into H_2. The option "H_2 addition" appeared, after evaluation, not to be a realistic alternative for the water-gas shift. The stream of H_2 that should be added would have to be so large (ranging from 17% to 69% of H_2 in final syngas stream) that it would be too expensive to purchase such a large stream. This means also that a large part of the final product is not produced but bought from another producer.

2.3.8. Evaluation of NON-KSI

Finally, all the non-Key Sustainability Indicators are determined for the winning case as well as for the benchmark process and a comparison is made between the winning case and the benchmark to check for any hotspots. In Figure 2.7 and Figure 2.8, the comparison between the benchmark and the winning case is given in circle and block logarithmic diagrams. The values of all indicators can be found in Appendix 2.12.
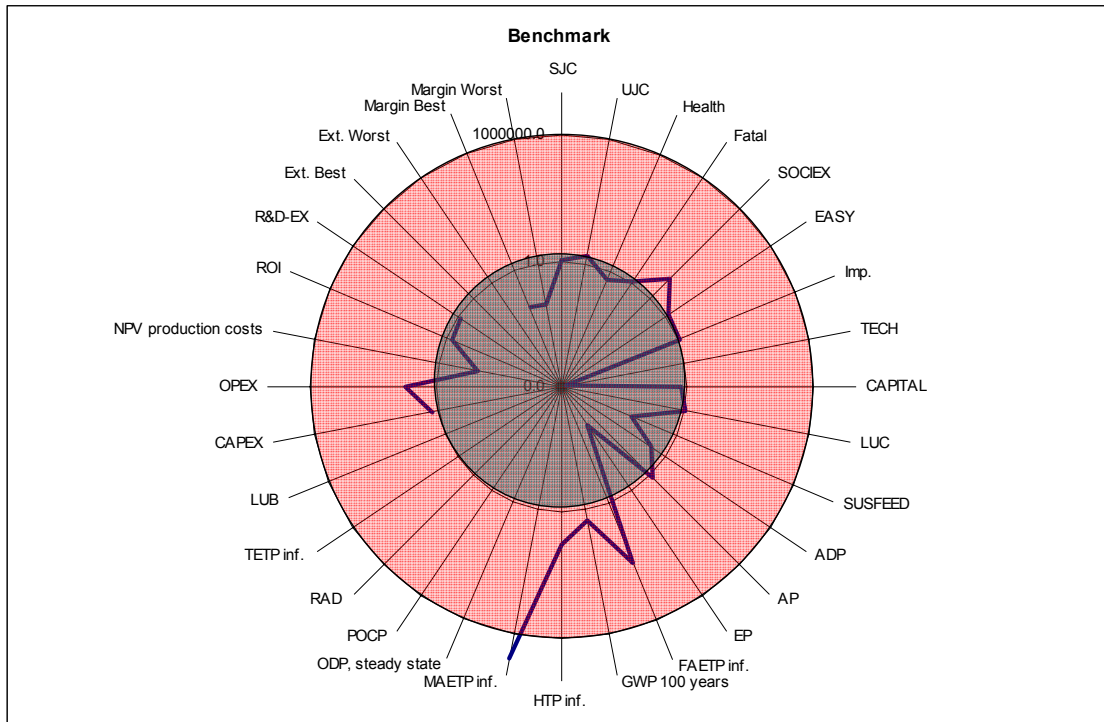
Figure 2.7: Circle diagram: Comparison all indicators between the benchmark and the winning case in logarithmic scale, *red area*: higher than the benchmark
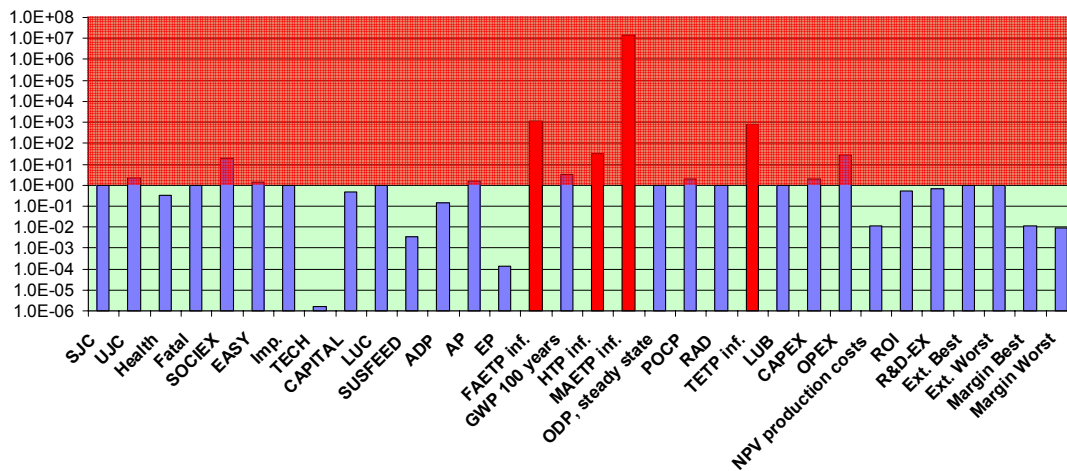
Figure 2.8: Block diagram: Comparison all indicators between the benchmark and the winning case in logarithmic scale, *red area*: higher than the benchmark, *red block*: planet indicator which is twice than the limit.

In order to take the error of the benchmark data or assumption into account, a limit is set when the indicator value becomes concerning. The limit is set to a value two times worse than then benchmark indicator value, where the non-KSI must be iterated or discussed.

From Figure 2.7 and Figure 2.8, several other indicators (besides the four which are red in Figure 2.8) of the winning case exceed this limit. For the People indicator "Room for SOCIALEX" and the Profit indicator "Operating Expenditure", this can be explained since both values depend strongly on the profit indicator "Capital Expenditure (CAPEX)". The "CAPEX" is calculated using estimation for the major equipment investment cost (Appendix 2.12). On the other hand, the "CAPEX" of the benchmark comes from investment data of SMDS Qatar, which is US$ 5 billion. Hence, these indicators cannot be compared with each other due to the different assumptions on the benchmark data from the literature ([15][16][17]).

Several planet indicators, red highlighted in Figure 2.8, exceed the limit. This can be explained by the fact that the data for the benchmark was not completely available. Since the Planet indicator values of each case differ slightly to each other, no iteration is needed to verify the winning case. It can be assumed that the results will not change.

2.3.9. Evaluation of KSI

Sustainable feedstock is a very important issue when a sustainable supply chain from biomass to syngas is required. The amount of biomass required to produce 8000 MW syngas, will influence the sustainability of the design.

The Global Warming Potential (GWP) is worse than the limit. The difference lies in the fact that the CO_2 emission of the winning case is still modelled as an emission. The possible intake of CO_2 from the air by the growth of biomass is not taken into account in the LCA calculation. When this is done, a lower value of GWP will be obtained. The

Human Toxicity Potential is also worse than the benchmark. This is caused by the availability of the benchmark data [18], which reports only large emissions, like sulphur, nitrogen, wastewater and carbon dioxide. Small amounts of the emissions of catalyst or solvent in the benchmark data [18] are not taken in to account.

The two chosen *Planet* indicators, the Global Warming Potential and the Human Toxicity Potential, are still good key indicators to select the best case from the different cases, since the differences of these KSI's are relatively large.

For the other two indicators, New Technology and Return on Investment; both are determined quantitatively for all cases. These indicators give also a good picture for each case to select the best case.

3. Basis of Design (BOD)

3.1. Description of the design

The subject of this Conceptual Process Design (CPD) as given in the project description is: "*The design of a life-cycle chain from biomass acquisition and transport to the production of Synthesis Gas for Shell Middle Distillate Products through large-scale gasification of biomass in the Rotterdam Harbour area.*"

So, the main objective of this CPD project is to design a sustainable logistics chain for the supply of biomass to Rotterdam and a sustainable chemical plant to produce syngas, a mixture of CO and H_2, with a H_2/CO ratio of 2 and a pressure of 40 bar at 500 K. The amount of syngas produced is equivalent to a LHV of 8000 MW, which totally serves as input for the Shell Middle Distillate Synthesis (SMDS) plant. The product specifications are given in Table 3.1.

Table 3.1: Desired product specifications of syngas

Impurity	Removal Level
H_2S + COS+ CS_2	< 1 ppmV
NH_3 + HCN	< 1 ppmV
HCL + HBr + HF	< 10 ppbV
Alkaline Metals	< 1ppbV
Solids (soot, dust, ash)	Essentially completely
Organic compounds (tars including BTX)	Below dew point
Class 2 tars: phenol, pyridine, thiophene	< 1ppmV
Objectives	**Desired level**
Production rate	334.3 kg/s
H_2/CO ratio	2
Inerts	below 5%

For the design certain issues are done:

- The process and option selection is considered as the main focus of this CPD project based on sustainability by applying two sustainability tools: CPD-SAT and SUSDAT.
- Other than just the process, the whole supply chain is regarded as the design project. This means that the logistic chain is also investigated.
- The software system GaBi 4 is used to create life cycle balances like LCA, LCC and SLCA, which were used in the sustainability tools.
- The social aspect and the role of the stakeholders of the process are investigated by surveys and discussion with experts, people from industry and stakeholders.
- Simulation of the biomass gasification process in the flowsheet modelling tool ASPEN PLUS.

and not done:

- Detailed design of the oxygen plant, wastewater treatment and Claus plant. Although these units fall within the system boundaries, they are not designed. These units are all standard, commercially available, units.
- Equipment design is not considered as the main focus of the design.
- The gasification reactor is not modelled with kinetics, since the data is still unknown and it is very difficult to define the biomass in ASPEN PLUS.

Therefore, conversion data from literature is used to set up the mass and heat balances around gasification reactor.

3.2. Process definition

In this section, the chosen process concept is explained and a block schemes is given to illustrate the chosen process concept. Furthermore, the applied thermodynamics and pure component properties are summarized.

3.2.1. Process Concept Chosen

Gasification to syngas comprises many reactions. The overall reaction of biomass gasification, as given in [67] is:

$$CH_{\alpha}O_{\beta}N + yO_2 + wH_2O \rightleftarrows x_1C + x_2H_2 + x_3CO + x_4H_2O + x_5CO_2 + x_6CH_4 + x_7N_2$$

$$\Delta H^0{}_{298} = -1.85 \text{ MJ kg}^{-1} \qquad\qquad (3.1)$$
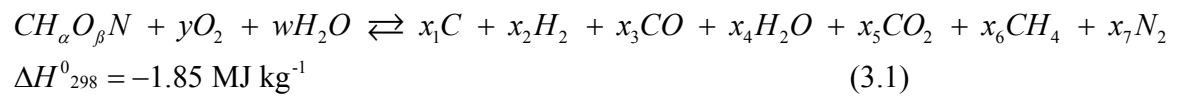
It consists of endothermic gasification reactions and exothermic (partial) oxidation reactions. The latter provide the heat required for the first reactions.

These reactions should take place on large-scale to produce 8000 MW of syngas. The word 'large-scale' into the project description almost immediately tells that the biomass gasification process should be operated continuously. This is also supported by the general guidelines about batch versus continuous processes.

Experimental data is used to calculate the gasification conversion, since the real kinetics of biomass gasification is still unknown [21] and the kinetic model from several literature sources [66] are difficult to model in programs like ASPEN PLUS. Thereby comes the fact that gasification consists of a series of reactions and that biomass (or wood) is not a clearly defined chemical substance, making kinetics even more difficult to model.

Numerous process options are possible for the gasification of biomass into syngas. The chosen option is selected with the use of two sustainability tools, viz. CDP-SAT, which is used to select the most sustainable feedstock options, and SUSDAT, which is used to select the most sustainable chain of unit operations (or tasks). In Chapter 5 more details of the selected process with its chosen unit operations will be given and discussed. In Chapter 2, the process options and the selection procedures are explained. All generated ideas for the process options and the differences between those options can be found in Appendix 2.

The selected design process consists of a logistics chain in the Baltic States and Scandinavia, where forest residues and sawdust are collected. This option is recommended by CPD-SAT. Forest residues are widely available for a relative low price and contain relatively less impurities and are well suited for transport. The wood residues are chipped and pelletised in the Baltic States and Sweden, since this reduces the volume to be transported enormously. It will save a lot of money on transport and also increases the sustainability of design since less energy is required to transport the wood residues.

TUDelft

In Rotterdam, the wood is gasified in a circulating fluidized bed (CFB) reactor, after which the resulting product gas is reformed to syngas in a monolith tar cracker. The CFB in combination with a monolith tar cracker using Ni catalyst consumes less biomass per unit of syngas than an entrained flow reactor. The gasification section is followed by a cooler, which indirectly generates electricity using a steam turbine, a sour water-gas shift (SWGS) reactor with CoMoS catalyst to adjust the CO/H_2 ratio, two stages desulphurizers with Zn/Ti sorbent inclusive their sorbent regenerator and a scrubber to remove the impurities from the syngas, an active coal filter and a CO_2-selective membrane to separate the CO_2 from the syngas. The sorbent is less hazardous and polluting than a solvent; this is also true for the CO_2-selective membrane.

3.2.2. Block Scheme

In Figure 3.1 a simple Process Flow Scheme is drawn. The PFS shows the total mass streams and yield of the process. The detailed PFS is given in Appendix 5.3. The overall thermal efficiency of the process is 87%.
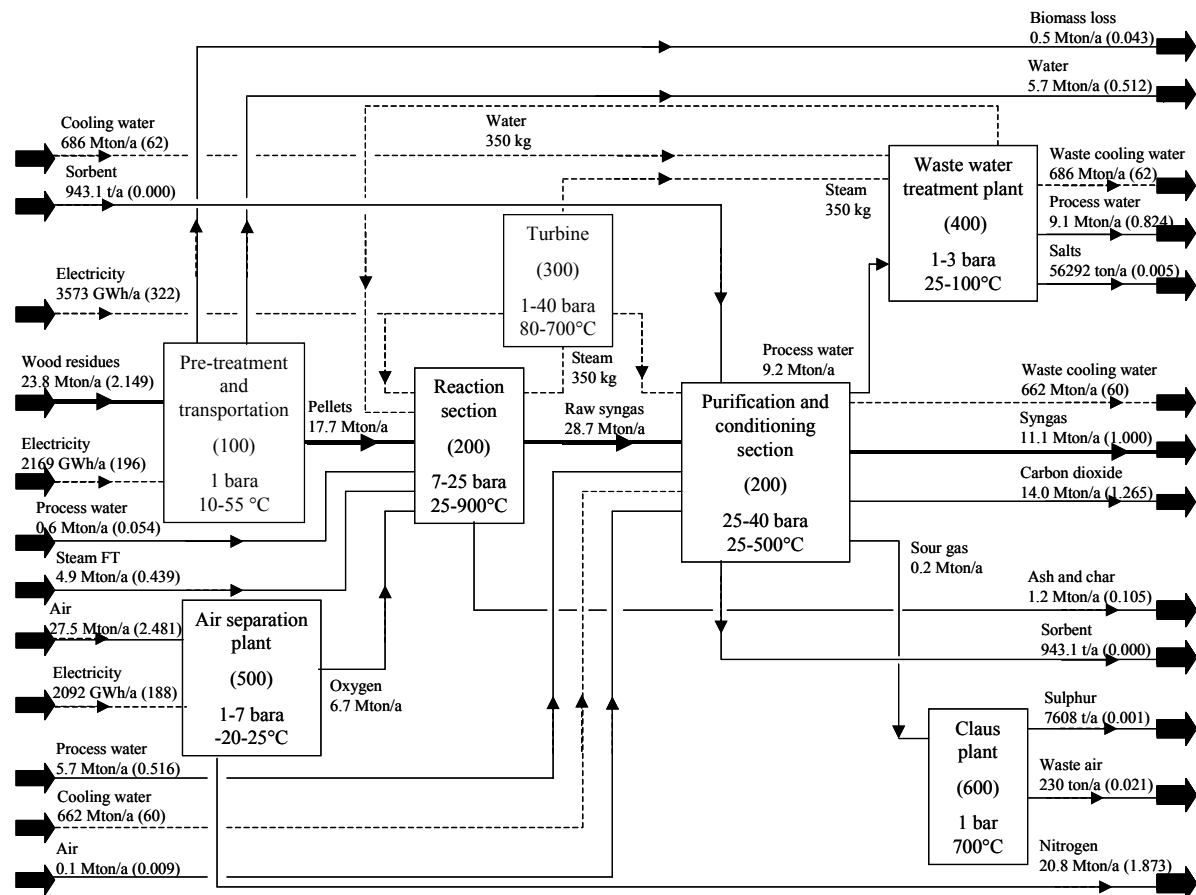
Figure 3.1: Simple PFS (Process water is recycled back into the plant, the difference between in and out is purged.)

For producing 8000 MW of syngas there are several process trains needed. This is schematically drawn in Appendix 3.1. It is impossible to produce the large quantity of

syngas in one process chain. From the equipment design in Section 8.2 it is concluded that there are 10 gasification reactors, tar crackers and gas coolers needed and 2 SWGS reactors, desulphurizer systems, NH_3/HCl scrubbers and CO_2-selective membrane.

3.2.3. Thermodynamic properties

For determining the thermodynamic (mixture) component properties of the process in Rotterdam the equation of state method is chosen for almost all unit operations. The equation of state method used describes both liquid and vapour phase behaviour. This method is applicable for systems, especially hydrocarbons, at high and moderate pressure and temperature. The equation of state model chosen is Peng-Robinson. The validity of this method is checked with data from literature and compared with data generated in ASPEN for simple systems. This validation is given in Chapter 4.7.

For reactions involving solids a special method is chosen, which is 'SOLIDS'. This method is used to model the sorbent reactions in the desulphurizers and the regenerator. The processes that only involve water (for example, the steam generated with the syngas cooler) are modelled with the 'STEAM-TA' model. More data on kinetics and equilibrium is given in Chapter 4.

3.2.4. Pure Component Properties

A list of the properties of the components, which are formed or used in the process, is given in Appendix 3.2.

3.3. Basic Assumptions

3.3.1. Plant capacity

The plant capacity is 8000 MW syngas, or 9.6 $Mton_{syngas}$/a without inerts. Feedstock of the process is forest residues and sawdust from Baltic States and Sweden. Base chemicals are oxygen, steam, process water, air and Zn/Ti-sorbents. The product is syngas and the by-product is sulphur. Waste is CO_2, nitrogen, salt, ash/dust/solids, water, spent catalyst, spent sorbent and wood loss.

The economical plant life is 20 years, based on data from practice [20]. The plant is designed for a production of 8000 hours/a. This number is based on refinery production hours. It requires an uptime of 91%.

3.3.2. Location

The location is fixed in the CPD assignment: Maasvlakte, Rotterdam, Appendix 3.3. The wood residues are collected from sites in the Baltic States and Sweden. The "Tweede Maasvlakte" is located at the coastline of the city of Rotterdam and therefore good accessible over sea and river. The plant area is estimated on data provided for the Shell Qatar-plant [16] at 1.5 km by 1.5 km.

3.3.3. Battery limit

In Figure 3.2 the supply chain is graphically represented. The supply chain is divided into two main processes: a logistics chain and a chemical plant. Each main process has its own battery limit, as given in dashed lines.

In the Baltic States and Sweden the wood residues are collected from several different sawmills and forests with trucks. The wood is chipped and pelletized and transported to the harbour. Large (Panamax) vessels transport the wood pellets to Rotterdam. This battery limit includes transport, chippers and pelletisers.
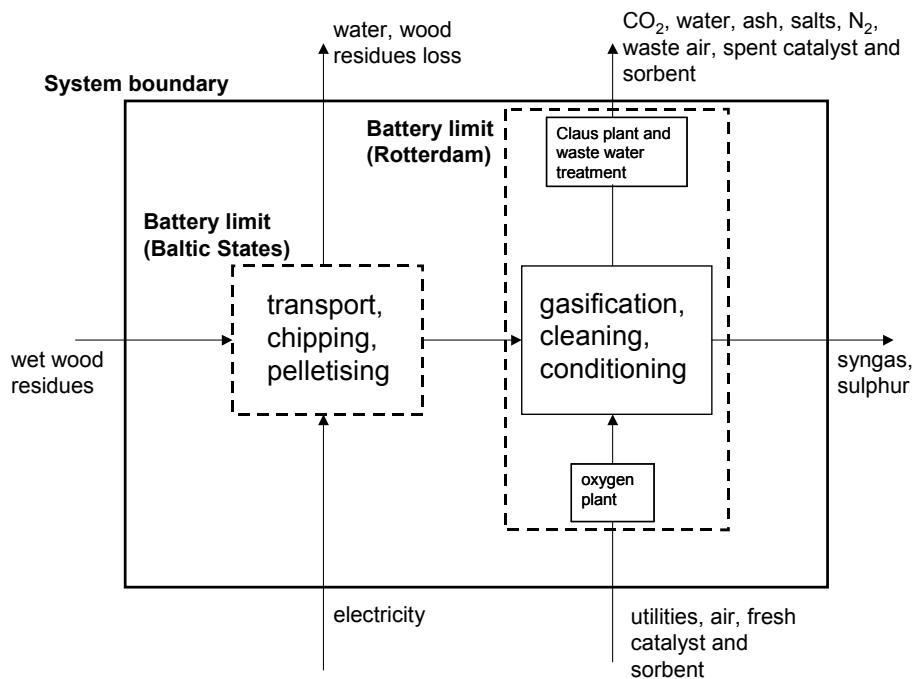
Figure 3.2 Battery limit of the process

In Rotterdam, the wood is gasified, cleaned from impurities and conditioned for the SMDS process. This battery limit includes gasifiers, tar crackers, gas purification units and gas conditioning units. It also includes an air separation plant, a Claus plant, an electricity plant and a wastewater treatment facility. Since the wastes from the chemical process cannot be put directly into the environment, they need to be treated first. The same reasoning also accounts for the oxygen. It is (thought to be) too expensive to purchase such large streams of pure oxygen, so an air separation plant is needed. However, these four plant units will be considered as a black box and will not be designed in detail.

3.3.4. Streams passing the battery limit

All streams and their properties crossing the battery limits are summarized in Appendix 3.4 and 3.5. Besides the continuous flows in and out of the process, there are certain streams, which will pass the battery limit periodically. These streams are: the monolith of

the tar cracker (1x in 5 years), the catalyst for the SWGS reactor (CoMoS) (1x in 5 years), the catalyst for the Claus plant (alumina) (1x in 5 years) and active coal (10 ton per year). The PFS in Appendix 5.3 and the block schemes only contain continuous flows, so the catalyst streams are not shown on these drawings.

3.3.5. Uncertainty in the design

During the design project, the uncertainty of the design is expected to decline according to general rule of thumb of design study. Usually a conceptual design has an uncertainty of 40% [14]. However due to the use of the two sustainability tools, CPD-SAT and SUSDAT the uncertainty will decline, since these two tools require a lot of data and accuracy on the design to make a decision based on sustainability. Therefore, the uncertainty in this design is estimated to lower than 40%. In Figure 3.4 the uncertainty in each design phase of this project is estimated.
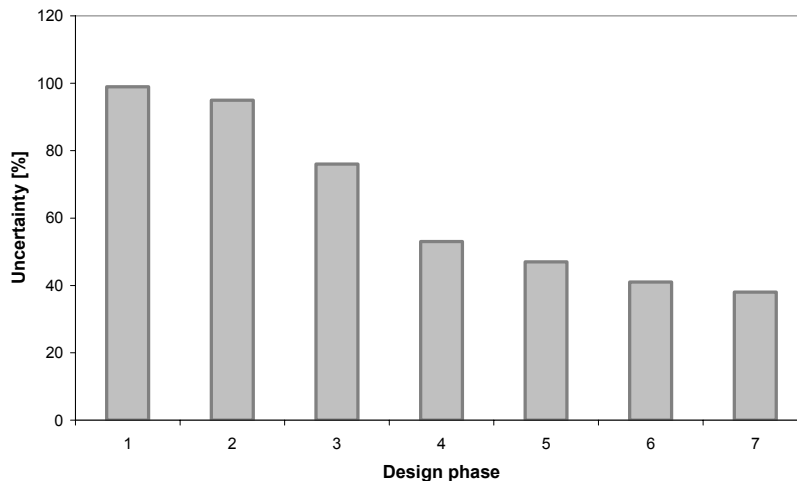
Figure 3.3 Uncertainty of the design process in time

3.3.6. Economic Margin

Margin = total value products OUT – total value IN as calculated for the review meeting was 400 M€. The economic margin as calculated at the end of the CPD is 1269 M€. The conclusion is that there is a large potential for profit in this process. The first margin was lower since other prices were used for biomass, oxygen and syngas and O_2 was bought instead of produced on site.

However, as will be cleared in Chapter 11, the economics of this process will depend much more on investment costs than on variable costs. The process is not economically viable unless equipment costs decrease, the government decides to subsidise the process, capital charges are lowered, energy efficiency increases and CO_2 is stored.

4. Thermodynamic Properties and Reaction Kinetics

Thermodynamics and kinetics are presented in this chapter. The operating window and validity of the thermodynamics and kinetics are discussed per chapter.

4.1. Circulating Fluidized Bed reactor (R201)

In developing a gasification theory, a simple thermodynamic model is often used assuming a gasification of pure carbon. Since the gasification process in a CFB occurs at temperatures ranging from 800 to 1100ºC, reaction rates are sufficiently high that modelling on the basis of the thermodynamic equilibrium of the main gaseous components and carbon (assumed as graphite) gives results that are close enough to reality that they form the basis of most commercial reactor designs [21].

In gasification a variety of reactions occur, of which some are endothermic and some are exothermic:

$$C + CO_2 \rightleftarrows 2CO \qquad \Delta H^0{}_{298} = +172 \text{ kJ mol}^{-1} \qquad (4.1)$$

$$C + H_2O \rightleftarrows CO + H_2 \qquad \Delta H^0{}_{298} = +131 \text{ kJ mol}^{-1} \qquad (4.2)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad \Delta H^0{}_{298} = +206 \text{ kJ mol}^{-1} \qquad (4.3)$$

$$C + \frac{1}{2}O_2 \rightleftarrows CO \qquad \Delta H^0{}_{298} = -111 \text{ kJ mol}^{-1} \qquad (4.4)$$

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2 \qquad \Delta H^0{}_{298} = -283 \text{ kJ mol}^{-1} \qquad (4.5)$$

$$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O \qquad \Delta H^0{}_{298} = -242 \text{ kJ mol}^{-1} \qquad (4.6)$$

$$C + 2H_2 \rightleftarrows CH_4 \qquad \Delta H^0{}_{298} = -75 \text{ kJ mol}^{-1} \qquad (4.7)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta H^0{}_{298} = -41 \text{ kJ mol}^{-1} \qquad (4.8)$$

The overall reaction of biomass gasification, as given in [67] is:

$$CH_\alpha O_\beta N + yO_2 + wH_2O \rightleftarrows x_1C + x_2H_2 + x_3CO + x_4H_2O + x_5CO_2 + x_6CH_4 + x_7N_2$$

$$\Delta H^0{}_{298} = -1.85 \text{ MJ kg}^{-1} \qquad (4.9)$$
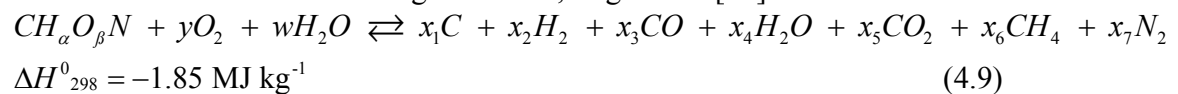
The desired operating temperature can be obtained by adjusting the exothermic and endothermic reactions. The reaction of wood with oxygen is always complete and exothermic; the reaction with steam or carbon dioxide is always endothermic and never complete due to thermodynamic limitations.

In this CPD, where a pressurised CFB is used with oxygen and steam, steam has the role of a moderator. In general, steam is used that is superheated to a temperature of 300-400ºC. A steam from the SMDS is used and heated to 490ºC in this CPD. The amounts of steam and oxygen in this model are based on data from literature [21].

The kinetics of gasification is not yet as developed as its thermodynamics. The kinetics is complicated due to the heterogeneous reactions and the complication of mass transfer phenomena due to the use of solid (porous) particles. The kinetics of coal gasification has been and still is a subject of intensive investigation.

The conversion of biomass consists of four steps: drying, pyrolysis, combustion and gasification. When entering the reactor, the wood particles start to dry rapidly, and a primary stage of reaction, namely pyrolysis, occurs. During this reaction wood is converted into gases, char, and tars. These processes are accompanied by gas production in the gas particle. The compositions of these products leaving the particle are mainly dependent on heating rate, biomass composition, ash content and composition, moisture content and size. These products are then further partly combusted with oxygen. After combustion, the remaining char is further gasified and several gas phase reactions, like the water-gas shift, reforming, polymerisation and cracking reactions, take place. These reactions are influenced by the gas phase composition, temperature, amount of oxygen and steam, bed material and residence time. Figure 4.1 shows the different reactions occurring during gasification [21].
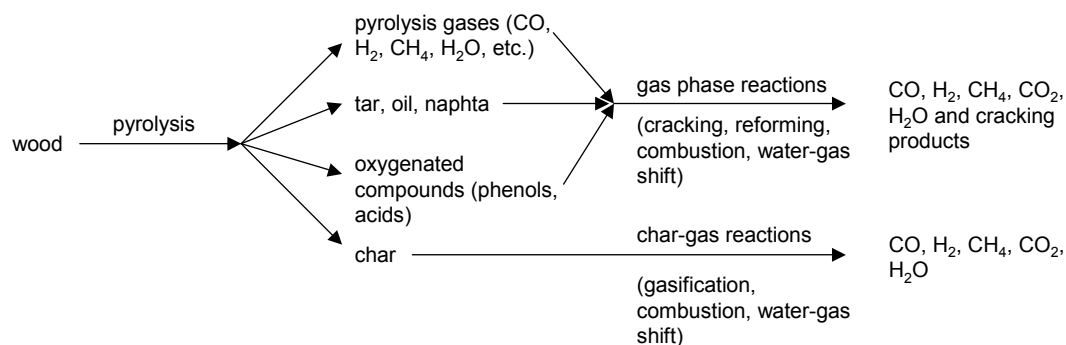
Figure 4.1: Reaction sequence for gasification of biomass [21]

The slowest reactions in gasification, and therefore the ones that govern the overall reaction rate, are the heterogeneous reactions with carbon surface: the Boudouard (4.1), the water gas shift (4.8) and the hydrogenation reactions (4.7).

4.2. Monolith Tar Cracker (R202)

The product gas leaving the CFB reactor contains CH_4, light hydrocarbons, tars and ammonia that are converted in the tar cracker. To simplify the model toluene is used as the tar model compound. The most important reactions in gas phase that take place, namely: the tar reforming (4.10), the dry tar reforming (4.11), the methane reforming (4.12), the water gas shift (4.13) and the ammonia decomposition reaction (4.14) are summarized below:

$$C_7H_8 + 7H_2O \rightleftharpoons 7CO + 11H_2 \qquad \Delta H^0_{1173} = 876 \text{ kJ mol}^{-1} \qquad (4.10)$$

$$C_7H_8 + 7CO_2 \rightleftharpoons 14CO + 4H_2 \qquad \Delta H^0_{1173} = 1105 \text{ kJ mol}^{-1} \qquad (4.11)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^0_{1173} = 227 \text{ kJ mol}^{-1} \qquad (4.12)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^0{}_{1173} = -33 \text{ kJ mol}^{-1} \qquad (4.13)$$

$$2NH_3 \rightleftharpoons N_2 + 3H_2 \qquad \Delta H^\circ{}_{1173} = 112 \text{ kJ mol}^{-1} \qquad (4.14)$$
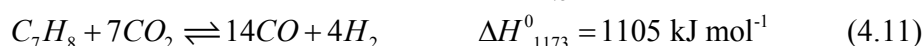
To counterbalance these endothermic reactions small part of the product gas (mainly CH_4 and light hydrocarbons) is combusted with oxygen. Nickel based catalyst (Ni/Al_2O_3) is proven to be very effective in decomposing tars, ammonia and methane in product gas at about 900 °C. Other known catalysts for tar cracking (for example dolomite) are only capable to convert tar, but not (or not at high conversion) ammonia. The reactor operates at about 900 °C, because:

- At lower temperatures the tar and ammonia decomposition rate is not high enough [22],
- At lower temperatures the catalyst deactivation rate by sulphur components in the product is too high [23],
- At higher temperatures more product gas should be oxidized to reach that temperature and as a consequence more CO_2 and H_2O is produced [24].

Thermodynamic equilibrium gas composition is achieved very rapidly with the nickel catalyst at this high temperature. Nevertheless the decomposition of tar and ammonia should be described kinetically. The decomposition rate of tar and ammonia can be assumed to be first-order [21]:

$$-r_i = k_i C_i \qquad (4.15)$$

The apparent reaction rate constant is described using an Arrhenius relation:

$$k_i = A_i e^{\frac{-E_{a,i}}{RT}} \qquad (4.16)$$

The pre-exponential factor and the activation energy for tar and ammonia decomposition are given by P. Simell [22] and presented in Table 4.1. The operating window is between 700 – 1000 °C.

Table 4.1: Pre-exponential factor and activation energy for tar and ammonia decomposition [22]

	A_i [m^3 kgcat^{-1} h^{-1}]	$E_{a,i}$ [kJ mol^{-1}]	R^2-(fit)
Tar	8.9·10^{10}	210	96
NH$_3$	1.5·10^{11}	220	87

It should be noted that this data generates an apparent reaction rate constant. This means that:

- It is specific for the composition of the product gas used in literature, and
- That is not possible to point out one reaction for which the reaction rate implies, a reaction network causes this rate.

The composition of the product gas in the literature [22] contains no H_2S, as is the case in this project for the gas leaving the CFB. Sulphur containing compounds deactivate the catalyst with regard to ammonia and tar decomposition. Sulphur decreases the ammonia decomposing activity more than the tar decomposing activity. At the applied conditions in the tar cracker (H_2S ~350 ppm, ~900 °C and ~6 – 7 bar) the activity of tar decomposition will not change. The conversion of NH_3 decreases for about 25% [23].

4.3. Sour Water Gas Shift reactor (R203)

The Sour Water Gas Shift (Sour-WGS) reactor is a reactor in which, besides the normal water gas shift reaction (WGS) [25], some other equilibrium reactions also take place [26]. The reactions in gas phase are the water gas shift (4.17), the HCN hydrolysis 1 (4.18), the HCN hydrolysis 2 (4.19) and the COS hydrolysis (4.20):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^{\circ}{}_{298} = -41 \text{ kJ mol}^{-1} \qquad (4.17)$$

$$HCN + H_2O \rightleftharpoons NH_3 + CO \qquad \Delta H^{\circ}{}_{298} = -332.9 \text{ kJ mol}^{-1} \qquad (4.18)$$

$$HCN + 2H_2O \rightleftharpoons CO_2 + NH_3 + H_2 \quad \Delta H^{\circ}{}_{298} = -91.1 \text{ kJ mol}^{-1} \qquad (4.19)$$

$$COS + H_2O \rightleftharpoons H_2S + CO_2 \qquad \Delta H^{\circ}{}_{298} = -34.6 \text{ kJ mol}^{-1} \qquad (4.20)$$
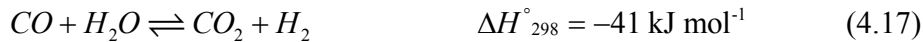
These reactions take place at high temperature (500 $^{\circ}$C) and catalyzed by a cobalt molybdate catalyst. The equilibrium constant (K_{eq}) curves as a function of temperature are plotted in Figure 4.2. This figure is constructed at 20 bar and it clearly shows that the HCN hydrolysis reactions will completely shift to the left at high temperature. The equilibrium constant for COS hydrolysis is plotted on the secondary axis and this equilibrium curve shows that at high temperature the equilibrium shifts to the left.
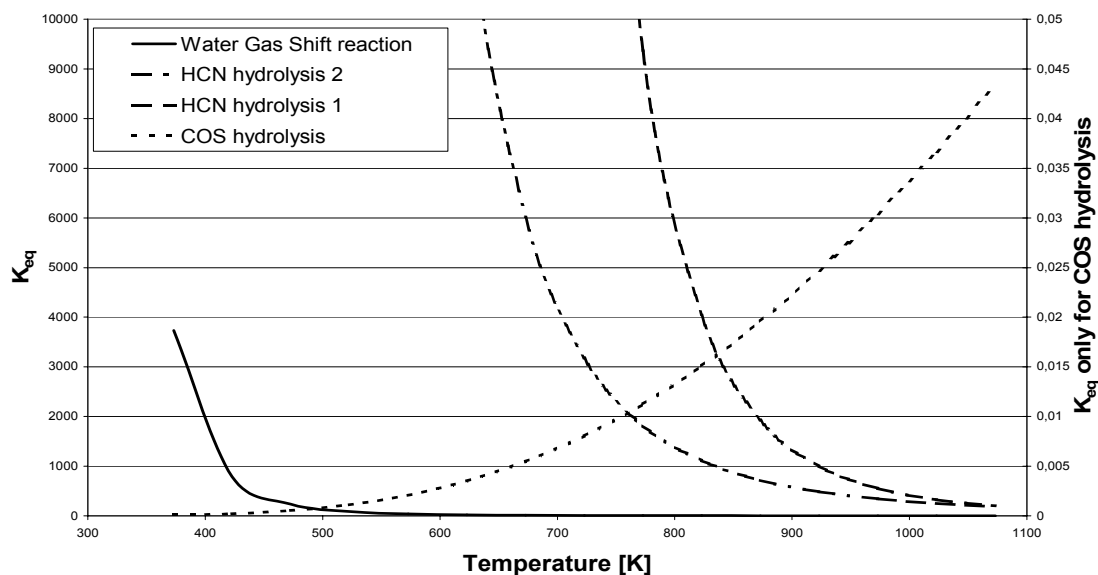
Figure 4.2: Equilibrium curves for reactions in SWGS reactor

Due to high temperatures the equilibrium concentration is quickly reached. Residence time of about 1.6 second is sufficient to reach equilibrium [27].

4.4. Bulk desulphurization and Zn/Ti sorbent regeneration

4.4.1. Bulk desulphurization

In desulphurization sulphur components (H_2S and COS) are removed from the gas stream due to the chemisorption on zinc titanate sorbent. The more reactive gas in the desulphurizer is H_2S, although a smaller fraction of COS is also present. The sulphidation reactions in the desulphurization section are the following:

$$\tfrac{1}{x}Zn_xTi_yO_{(x+2y)}\ (s)+H_2S\ (g)\rightarrow ZnS\ (s)+\tfrac{y}{x}TiO_2\ (s)+H_2O\ (g) \qquad (4.21)$$

$$\tfrac{1}{x}Zn_xTi_yO_{(x+2y)}\ (s)+COS\ (g)\rightarrow ZnS\ (s)+\tfrac{y}{x}TiO_2\ (s)+CO_2\ (g) \qquad (4.22)$$
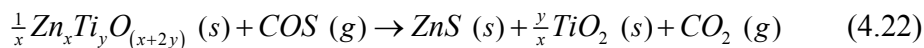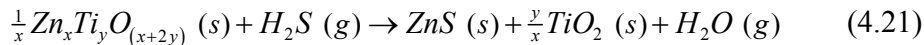
The kinetics for the sulphidation reaction depends strongly on the catalyst. As base the catalyst data from [30] is used. The experiments in literatures ([28] [29] [30]) is performed in similar temperature ranging from 450 – 650 °C. The pressure effect on the performance of the sorbent is said to be minimal [31]. This indicates that the data can be used for the modelling. The sulphidation reaction of zinc titanate is modelled using the 'Unreacted Shrinking Core (USC) Model'. The USC model is usually preferred for modelling purposes due to its simplicity [28].

The sulphidation reaction in the bulk desulphurizer is controlled by the surface reaction rate and the diffusion through the product layer. The mass transfer through the product layer will start to control the sulphidation rate after about 5 mol% fractional sorbent conversion [29]. The diffusion through the product layer at 500 °C is very small [29] that after the product layer formation the sulphidation rate is negligibly small. To simulate this behaviour, it is assumed that only 5 % of the sorbent reactive surface area is reacted. This simplification can be justified, referring to the literatures ([30] [29]) that have similar results. This is given graphically in Figure 4.3. It can be seen that the simplified kinetics used and literature value is very comparable.
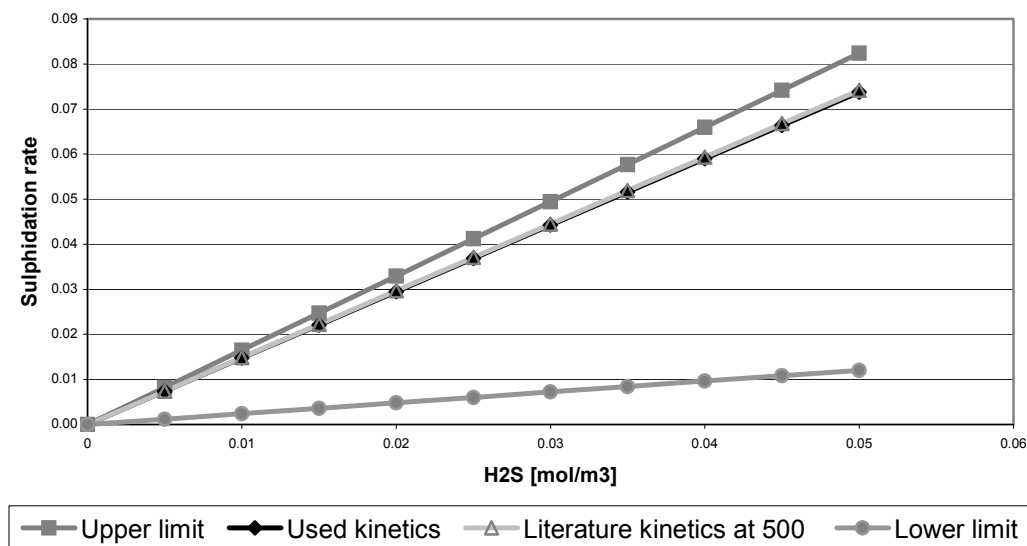
Figure 4.3: Graphical representation of the kinetics used

TUDelft

The kinetics of the surface reaction, which is 1st order in H_2S concentration, are described using an Arrhenius type expression, see section 4.2, and is summarized in Table 4.2.

Table 4.2: Pre-exponential factor and activation energy for the USC model [30]

Model	A_i [s^{-1}]	$E_{a,i}$ [kJ mol^{-1}]	Reactor
USC	0.347 × reactive surface area	27.312	Transport reactor

The pre-exponential factor is dependent of the reactive surface area of the particles. In Table 4.3 the Arrhenius pre-exponential factor at different reactive surface area is given.

Table 4.3: Reactive surface area and Arrhenius pre-exponential factor bulk desulphurization [30]

Particle size [µm]	Reactive surface [m^2 m^{-3}$_{reactor}$]	Reactive surface (diffusion effect) [m^2 m^{-3}$_{reactor}$]	A_i [s^{-1}]
100	8659	433	150
130	6660	333*	116*
160	5412	271	94

* used in modelling

Considering the COS, it is assumed that the reaction rate is the same as H_2S. This assumption is derived from the mass balance calculated in [31].

4.4.2. Zn/Ti sorbent regeneration

The main reactions of the sorbent regeneration are:

$$ZnS\ (s) + 1.5O_2\ (g) \rightarrow ZnO\ (s) + SO_2\ (g) \qquad (4.23)$$

$$xZnO\ (s) + yTiO_2\ (g) \rightarrow Zn_xTi_yO_{(x+2y)}\ (s) \qquad (4.24)$$
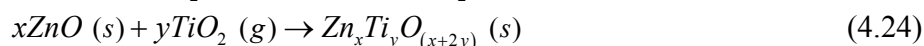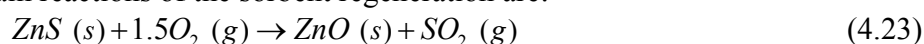
Individual oxides are assumed to form the original zinc titanate. At regeneration condition the undesired zinc sulphate can also be formed according to the following reaction:

$$ZnO\ (s) + SO_2\ (g) + 0.5O_2\ (g) \rightarrow ZnSO_4\ (s) \qquad (4.25)$$

The rate of oxygen to form the zinc sulphate in comparison to the rate of SO_2 release can be considered to be insignificant [32].

The regeneration reaction is 2nd order in oxygen concentration and shown to be kinetically controlled. The Arrhenius expression of the kinetic is summarized in Table 4.4.

Table 4.4: Pre-exponential factor and activation energy for sorbent regeneration

A_i [m^3 mol^{-1} s^{-1}]	$E_{a,i}$ [kJ mol^{-1}]	Reactor
8.36·10^7	201.740	Entrained flow reactor

The temperature-operating window for the regeneration section is quite small, namely 700 – 800 ºC [32].

4.5. Ultra desulphurization

The same zinc titanate is also used in the ultra desulphurization. The kinetic discussed in the bulk desulphurization section will also apply. The mean sorbent size in the ultra desulphurization is approximately 20 μm with higher reactive surface area, which will increase the sulphidation rate. But, the inlet gas flow will also carry the elutriated sorbent particles from the bulk desulphurizer into the ultra desulphurizer. Large portion of these sorbent particles are inactive. It is assumed that only 50% of the sorbent is active. The Arrhenius pre-exponential factor for 20 μm sorbent particles is tabulated in Table 4.5.

Table 4.5: Reactive surface area and Arrhenius pre-exponential factor in ultra desulphurization [30]

Particle size [μm]	Reactive surface [m^2 m^{-3}reactor]	Reactive surface (diffusion effect) [m^2 m^{-3}reactor]	A$_i$ (50%) [s^{-1}]
20	43295	2165*	375*

* used in modelling

The sorbent out of the reactor will be directed to the regenerator where it will be regenerated together with the sorbent from the bulk desulphurizer.

4.6. NH₃/HCl Scrubber

In the aqueous scrubber mainly ammonia (NH$_3$) and hydrogen chloride (HCl) is transferred between the two phases and absorbed by a liquid water stream. There are several ways to describe the solubility of a gas in water. The Henry's law constant is defined as [33]:

$$k_H = c_i / p_i \qquad (4.26)$$

A simple way to describe Henry's law as a function of temperature is:

$$k_H = k_H^0 \exp\left(\frac{\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right) \qquad (4.27)$$

where $\Delta_{sol}H$ = enthalpy of solution. The temperature dependence is:

$$\frac{-d \ln k_H}{d(1/T)} = \frac{\Delta_{sol}H}{R} \qquad (4.28)$$

The relation between the equilibrium ratio or K-value of separation and the Henry's law constant is [34]

$$K_i = \frac{y_i}{x_i} = \frac{H}{P} \qquad (4.29)$$

where $H = \dfrac{55.3}{k_H}$.

The Henry's Law constant at standard conditions and the temperature dependence of ammonia and hydrogen chloride are tabulated in Table 4.6 [33].

Table 4.6: Henry's law constant at standard conditions and temperature dependence of NH$_3$ and HCl [33]

	NH$_3$	HCl
k_H^0 [M/atm]	58	19
$\dfrac{-d \ln k_H}{d(1/T)}$ [K]	4100	9000

This standard method is frequently used in designing stripping/absorbing system and is valid for the operating window of the process.

4.7. Property estimation of component mixtures

Three methods for calculating phase equilibriums are distinguished (by ASPEN flowsheet simulation): The equation of state method, the activity coefficient method and a special application method.

For modelling the process in Rotterdam the equation of state method is chosen for almost all unit operations. The equation of state method used describes both liquid and vapour phase behaviour. This method is applicable for systems, especially hydrocarbon, at high and moderate pressure and temperature. The equation of state model chosen is Peng-Robinson.
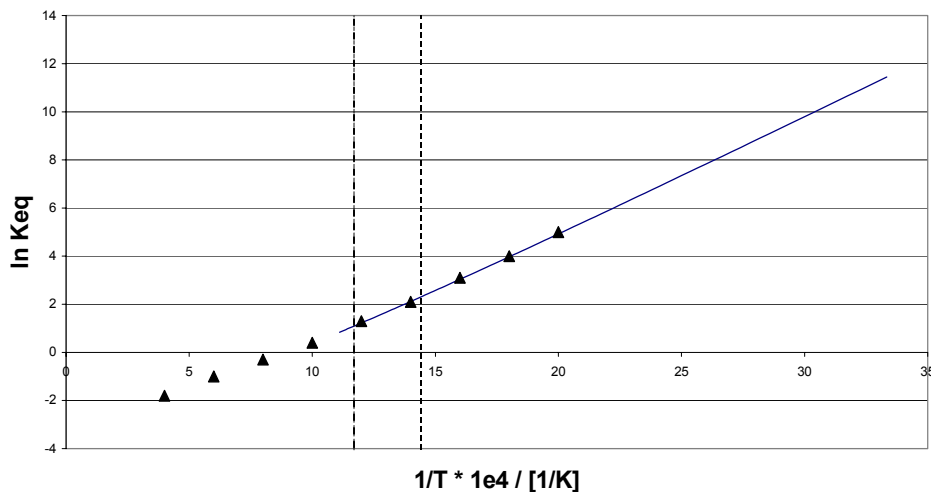
Figure 4.4: Equilibrium constant for the WGS reaction

As validation for the use of Peng-Robinson the data generated in ASPEN PENG-ROB model is compared to the literature. Taking the water gas shift reaction as an example (4.19), the ASPEN generated data is compared to data in Smith et al. [19] (page 569). The comparison is plotted in Figure 4.4, where the literature data is depicted as triangles and the ASPEN data as solid line. The two sets of data correspond excellently, also in the operating window of the (sour) water gas shift that is the area between the dashed lines. This gives an indication about the validity an accuracy of the Peng-Robinson model.

5. Process Structure & Description

5.1. Criteria and selections

The sustainability characteristic and performance aim of the design bring along some important aspects with it. Aspects like heat integration and equipment selection.

In section 2.3 the process chain chosen using SUSDAT is discussed. Not all unit operations in this scheme are specified as equipment. This chapter will also discuss the transformation from the winning case after SUSDAT to the choice of equipment in the final design. The equipment selection will be discussed and the design variables/criteria will be given per equipment of the pre-treatment step and the gasification of wood residues to syngas.

5.1.1. Chipping, pelletising and transportation of wood residues

The pre-treatment step of the block scheme, chosen using SUSDAT, was taken into further consideration. This step was thought not to be optimal for the total supply chain. In the pelletising step the density of the chips is increased roughly with a factor 3 (pellets of 10 mm diameter x 30 mm length are made) and the water content is reduced to 7 wt-% in one equipment. Instead of pelletising also steam -, oven -, and fluidized bed drying are considered as possible options to pre-treat the wood residues. Therefore a comparison is made based on the characteristics of the different processes, like the economics and transport. The comparison is tabulated in Table 5.1.

Table 5.1: Comparison of different drying methods

Drying step	No. drying equipments[1]	Investment costs [M€]	Electricity price [M€]	No. of ships for transport[2]	Transport costs [M€/a]	Total costs over 20 years[3] [M€]
Pelletising	497	413	139	236	72	5055
Steam	71	376	338	658	202	11541
Oven	25	125	76	658	202	5801
Fluidised bed	171	239	278	658	202	10081

Two major conclusions can be drawn from Table 5.1. First, due to the densification of the pelletising step the number of ships is about three times smaller. This would mean a big positive impact on LCA issues. The second issue is the total cost over a period of 20 years. It is clear that compared to conventional drying steps the pelletising step is economically more attractive. Thus the pelletising step, besides previous ideas, is proven to be the better option and maintained in the total chain.

The collection, pre-treatment and transportation chain as given by SUSDAT has a number of variables, which determines the validity of its choice.

The first one is the availability. Wood residues from harvesting wood and wood industries were chosen. These residues are found in the Baltic States and Sweden and a rough estimation of available amounts is given in Table 5.2.

---

[1] Based on a total transport of 19.9 Mton/a
[2] Based on a density of 650 kg/m^3 for the pellets and 240 kg/m^3 for the chips
[3] Lifetime varies from 10 to 15 years, so al equipment has to be replaced once

Table 5.2: Estimated available quantity of wood residues in different countries in 2003 [35]

Biomass source	Annual quantity	
	[1000 m^3]	[Ton][4]
Baltic States	29.990	11.996.000
Estonia	*10.500*	
Latvia	*13.260*	
Lithuania	*6.230*	
Sweden	69.300	27.720.000

About 23.8 Mton of biomass is needed to produce 8000 MW of syngas. So it is clear that there is enough biomass available in the chosen region. Wood residues have a supply window of 9 months and wood residues form industrial activities (sawdust) have a supply window of 12 months. This means that a whole year supply of wood, to the plant, is possible, when a large storage is build in the Baltic States and Sweden and a medium storage is placed in Rotterdam.

The second variable is the gathering of these wood residues. As stated above, woody residues are formed at industrial facilities (saw mills) and at harvesting sites. For the first site this means a fixed location where additional equipment can be placed for the further treatment of the residues, e.g. chipping and pelletising. However the second location is a dynamic location, which means that it will be impossible to place additional equipment for further treatment. So these residues will be gathered and transported to a central storage facility. At these facilities it will be possible to chip and pelletise the residues.

The third variable is transportation of the pellets to the Rotterdam harbour area. Three major options exist, transport by train, truck or ship. The first option is cancelled due to the large volume that has to be transported. So the obvious option is transport by ship, because the plant will be build near the coast and the chosen countries all have a large shore and good access to harbours. Trucks will be used to transport the pellets to the harbours and ships will transport the pellets to Rotterdam. The advantage of pellets above chips is the density increase with pellets, so less volume is needed to transport an equal amount of wood. This translates to less ship.

The fourth variable is the storage. The storage can be divided over multiple points, since wood is imported from 4 countries and to provide sufficient back up in case of less supply. An indication on how this can be realised is given in Figure 5.1 together with the supply chain. The squares are storage locations at harbours and the circles are gather/storage locations spread over the countries, where chipping and/or pelletizing takes place. Figure 5.1 schematically shows 30 storage facilities at sawmills (260,000 m^3), 30 storage facilities for forest residues (7.000.000 m^3) and 10 silos at the complex in Rotterdam (430,000 m^3). The calculation for the estimation of the storage facilities is given in Appendix 5.1. These storage facilities provide a back up of about 4 months.

---

[4] Wood density = 400 kg/m^3 [25]

TUDelft

Figure 5.1: Fictive representation of the supply chain

5.1.2. Circulating Fluidized Bed reactor

The choice of reactor is done on advice of the outcome of SUSDAT. As can be seen in Section 2.3, numerous process configurations for the conversion of biomass to syngas are possible. The outcome of SUDAT was that the most sustainable process chain, was a chain with a pressurised CFB, operating on pure oxygen and steam.

Important design criteria for a CFB are the choice between atmospheric pressure or elevated pressure, and the choice between using air or oxygen. Using a pressure of 7 bar in the gasifier and later on in the process going up to 40 bar has the advantage that compressors can be used without an intercooler. Increasing the compression ratio will result in too high temperatures, and therefore in the need of expensive and inefficient intercoolers [36]. Another advantage of elevated pressure is the reduced size of the equipment. Using oxygen has the advantage that there is no dilution of the syngas by nitrogen. Important here is also that the project objective stated that there could be no more than 5% inert in the product syngas stream. Also the equipment can be a lot smaller with oxygen. Disadvantage is that an (expensive) oxygen plant is needed.

Fluidized bed gasifiers offer good mixing and therefore it is inevitably that a part of the partially reacted biomass is removed with the ash at the bottom of the reactor. This places a limitation on the carbon conversion of the CFB. However, some pressurised fluidized bed processes to date have achieved a carbon conversion of 99% [21].

The most complex part of the design of a CFB is the fluidisation. A CFB operates in a fluidisation regime where, the difference in velocity between gas and solids (also called the slip velocity) is as high as possible. Gas velocities range from 5-8 m/s. Oxygen and steam are used as the fluidisation and gasification medium. When they enter the gasifier below the solid bed, the gas velocity should be high enough to fluidise the particles in the bed.

TUDelft

Attention has to be paid to the sizing of the particles in the feed; too small particles will become entrained in the bed and leave the bed at the top with the syngas. The particles entering the CFB have a dimension of 1×3 centimetres. An internal cyclone can partially capture these particles and return them to the gasification bed.

The CFB has to be operated below the softening point of the ash, which is typically 800-950°C for biomass. Above this temperature, the ash starts to soften sufficiently so that the individual particles begin to agglomerate. These larger particles will fall to the bottom of the bed, and their removal will cause a considerable problem. Another problem of the ash is, that it is extremely aggressive in terms of corrosion owing to the high salt content when it melts.

The design of the CFB is based on literature values and practical experience. The operating condition and design criteria of the CFB are summarized in Table 5.3.

Table 5.3: Design criteria and operating condition of the CFB

Operating conditions	Design criteria
Operating temperature	800 – 950 °C
Operating pressure	7 bar
Exit volumetric gas flow	517 m^3/s
Gas velocity	5 – 8 m/s
Particle size	1×3 cm

5.1.3. Candle filter

The choice of a candle filter after the CFB is not that obvious, because the outcome of SUSDAT was based on a cyclone. However further investigation of a cyclone showed that there are two major sort of cyclones, the high efficiency and the high throughput cyclone. In the winning case the high throughput cyclone is needed and this cyclone cannot remove the smallest particles. These particles can cause problems in the tar cracker, thus they need to be removed completely. A candle filter is a more sophisticated system that can practically remove all particles up to 1 μm. The operating condition and design criteria of the candle filter are summarized in Table 5.4.

Table 5.4: Design criteria and operating condition of the candle filter

Operating conditions	Design criteria
Inlet gas temperature	800 – 900 °C
Operating pressure	7 bar
Volumetric gas flow	517 m^3/s
Filter face velocity	0.01 – 0.06 m/s
Particulate loading	< 10000 ppm
Backpulse system pressure	Up to 56 bar
Backpulse duration	Up to 1 s
Pressure drop	Up to 1 bar

5.1.4. Monolith tar cracker

From SUSDAT the main task of the catalytic tar cracker is to remove the tars from the product gas stream exiting the CFB. The tar cracker is also able to reduce the ammonia level in the gas stream up to some extent.

TUDelft

Catalytic tar cracking takes places in an external bed, not internal in the CFB reactor. When the nickel-based catalyst is put in the CFB reactor, it is surrounded by char that deactivates the catalyst very rapidly [37]. Catalytic tar cracking is therefore performed either in fixed (packed bed or monolith) or fluidised external bed. The temperature required for this type of operation is around 900°C and thus situated preferably close to the gasifier outlet.

A critical problem for using catalysts in the gasification process is fouling and plugging by particulates. This problem can be solved by using the catalyst in the fluidised bed or in the shape of monolith.

Fluidized bed is an excellent type of reactor with good temperature distribution. Fluidized beds require smaller catalyst particles that are more vulnerable to attrition and deactivation. Keeping the catalyst in the reactor is also an issue; this will require a cyclone or some sort that introduces more costs.

A monolith on the other hand is relatively cheaper. The open channels make sure that low pressure drop is maintained. The catalyst is deposited as thin layer on the channel surface where no solid-to-solid friction occurs, like in a fluidized bed. Attrition that leads to deactivation is minimal.

Due to these reasoning a monolith reactor with Ni/Al_2O_3 catalyst, typically used for catalytic cracking, is chosen. Compared to packed bed reactor, monolith gives comparable CO and H_2 yield but slightly less methane and ammonia conversion [23]. The ammonia level from the tar cracker has to undergo further reduction anyway to reach the level under 1 ppmV, despite the choice of reactor. With reference to the product specification, the level of methane is not too crucial for the process since is can be seen as inert. Further, the application of a monolith reactor could have its advantage in sizing the reactor since the pressure drop in a monolith is lower relative to a packed bed reactor.

The operating condition and design criteria of the tar cracker are summarized in Table 5.5.

Table 5.5: Design criteria and operating condition of the tar cracker

Operating conditions	Design criteria
Inlet gas temperature	900 °C
Operating pressure	6.3 bar
Volumetric gas flow	782 m^3/s
Residence time	0.2 – 0.3 s
Catalyst	Nickel/Al_2O_3
Conversion of tars	99.9 %
Exit ammonia concentration	As low as possible
Pressure drop	Up to 1 bar

5.1.5. Syngas cooler

Since the hot gas cleanup for sulphur components (desulphurizers) works at temperatures considerably lower than the tar cracker exit temperature, it is necessary to cool the syngas before it enters the bulk desulphurisation unit. The cooler produces high-pressure steam, which is used to generate electricity in a steam turbine. There will be one syngas cooler after each tar cracker.

Two aspects of gas cleaning are very important when designing a syngas cooler; particle removal and condensation from tars or ash. It is assumed that almost all the particles, tars

and ash have been removed before the syngas cooler, either in the candle filter or the tar cracker.

The heat transfer inside the cooler takes place through a number of coils. The hot syngas passes through the shell and steam from the FT process flows through the coils. The syngas is cooled from 900 to 200 ºC, before further compression to 25 bars, while pressurized water is heated from 80 to 685 ºC.

5.1.6. Sour water gas shift reactor

The main purpose of water gas shift reactor is to adjust the H_2/CO ratio to 2. SUSDAT showed the WGS reactor after the gas cleaning section. Relative to the winning case of SUSDAT the location of the WGS reactor in the syngas cleaning train is changed. The WGS is placed after the tar cracker due to temperature level consideration at the end of the process chain. Using low temperature shift at the end of the chain means warming up the gas stream after gas cleaning, which has to stay at low temperature before compression without intercoolers. Furthermore, low temperature shift is more suitable for syngas production used in methanol or ammonia processes where almost all CO is converted in H_2. The shift reaction has a high equilibrium constant at low temperatures compared to high temperatures as is showed in Figure 4.2, but the equilibrium will be reach slower at lower temperature.

The catalyst used is the cobalt molybdate (CoMoS) [26] with a density of 600 kg/m^3. This catalyst is active in its sulphided state and takes advantage of the relative high sulphur level in the gas stream out of the tar cracker. Due to the high sulphur level this type of WGS is also called the sour gas shift (SWGS) or raw gas shift.

Another reason for selecting the sour water gas shift reactor is the ability to convert impurities to better removable compounds, see HCN and COS hydrolysis reaction in Section 4.3. At high temperatures the HCN is almost completely removed and a large amount of COS is converted to H_2S. The SWGS reactor is advantageous for the downstream processing of the syngas.

From literature, it became clear that for the WGS reactor an adiabatic fixed bed reactor is a common practise [25]. Since the difference between the SWGS and the WGS reactor is only the catalyst the same operation mode is chosen for the SWGS.

Since no accurate kinetic data of the SWGS is known the most variables are set, so the only design variable is the temperature in the reactor. Residence times of about 2200 h^{-1} are sufficient to reach equilibrium [27].

The operating condition and design criteria of the SWGS are summarized in Table 5.6.

Table 5.6: Design criteria and operating condition of the SWGS

Operating conditions	Design criteria
Operating temperature	470 – 530 °C
Operating pressure	25 bar
Volumetric gas flow	127 m^3/s
Residence time	1.6 s
Catalyst	Cobalt molybdate (CoMoS)
Catalyst bed voidage	0.4
Pressure drop	20 % reactor pressure

5.1.7. Bulk desulphurizer and Zn/Ti sorbent regenerator

From SUSDAT desulphurization takes place in two stages sorbent desulphurizers. However, in SUSDAT another alternative is not taken into account, namely simultaneous gasification and desulphurization in the CFB. Therefore, the choice of desulphurization between dolomite (or other Ca-based catalyst) in the CFB and a separate bulk desulphurization unit will be reviewed first in this section. Both have their advantages and disadvantages.

The lower sulphur level due to dolomite utilization does not lead to radical change in the performance of the tar cracker. The extra ammonia conversion that can be gained does not lead to significant advantage for the following gas-cleaning units. The main disadvantage of utilizing the dolomite is the large amount of solid waste that has to be dealt with. Fast calculation gives an amount of approximately 23.4 tons dolomite per hour. Regeneration methods are available, for example grinding and recycling the spent dolomite can lead to 18 % reduction of the solid waste [38]. Utilization of the dolomite in CFB is a very cost effective option. The extra investments needed for the regeneration option is also minimal.

The bulk desulphurization process uses regenerable sorbent. Due to the regeneration, the solid waste generated is a factor 10 smaller than the dolomite option. This option leads to much cheaper solid waste treatment and handling. On the other hand, utilization of a bulk desulphurization unit will need extra investment for the desulphurizer and regenerator vessels. A Claus unit is also necessary to treat the sulphur components to produce elemental sulphur. Extra investments are also necessary for the Claus plant while the market value for elemental sulphur will bring extra income for the process. This option is less cost effective compare to the dolomite option.

Although the solid waste can be used as landfill, another factor must also be taken into account. In designing a sustainable process, it is very important that the process also has a 'sustainable' image. The amount of waste generated should therefore be minimized; a sustainable process does not produce too much waste. This is the reason of choosing the more expensive option, a separate bulk desulphurization.

The reactor alternatives for bulk desulphurizer and sorbent regeneration are:
- Transport reactors
- Fluidized bed reactors
- Moving bed reactors

The choice falls on the transport reactor due to the following advantages of this reactor type over fluidized bed and moving bed reactor:
1.   Less sorbent inventory due to higher solid circulation
2.   Less sulphur absorbed and regenerated per cycle
3.   Less sorbent exposure to reactive environment both in desulphurization and regeneration

Transport reactors are operated at relatively high gas velocity (8 – 20 m/s), this to make sure that the fluidization characteristics are made. Physical properties (e.g. hardness) of the sorbent will be the upper constraint of gas velocity. To minimize attrition and

TUDelft

premature deactivation of the sorbent, velocity of 10 m/s is assumed to be the optimal gas velocity.

To make sure of sufficient regeneration the gas velocity of 6 m/s [31] in the regenerator is assumed. The height to gas velocity ratio is also fixed as in the desulphurizer. This will bring the system to fast fluidization regime where entrained flow is achieved. In this regime the reaction bed is denser and the solid will have larger residence time than in a transport reactor in the pneumatic flow regime.

Another important parameter in fluidization is the particle size. Smaller particles are required for fluidized systems. Particle size ranging from 100 – 160 μm is typical for this type of reactor. As base for the calculation a particle size of 130 μm is assumed.

The utilization of the transport reactor leads to loss of sorbent due to attrition. The sorbent loss is assumed to be approximately 0.03% [31] of the sorbent in the riser.

The bulk desulphurization operates at approximately 500 °C in a transport reactor [31]. The spent sorbent is regenerated at approximately 750 °C in an entrained flow reactor where the sulphur components are released and sent to a Claus unit [31]. The main goal of the bulk desulphurization is to reduce the sulphur components level in the syngas down to 20 ppmV. This desulphurized syngas will then be sent to the ultra cleaning section where the syngas specification will be achieved.

The main criterion for the sorbent selection is regeneration. The regeneration rate has to be faster than the sulphidation rate to make sure that continuous sorbent circulation does not lead to decreasing performance. Other important aspect is the physical property of the sorbent particle that has to withstand harsh condition during the desulphurization and regeneration cycles. Zinc-based sorbent are proven to be the most suitable sorbent to be used in desulphurization technology. The development of zinc titanate sorbent is presently the most promising and these types of sorbent are used/tested continuously in pilot plants worldwide. Due to these facts the zinc titanate will be used to complete the desulphurization task in the process.

The operating condition and design criteria of the bulk desulphurizer and regenerator are summarized in Table 5.7 and Table 5.8 respectively.

Table 5.7: Design criteria and operating condition of the bulk desulphurizer

Operating conditions	Design criteria
Operating temperature	480 – 520 °C
Operating pressure	21 bar
Volumetric gas flow	165 m³/s
Gas velocity	8 – 20 m/s
Sorbent type	Zinc titanate
Sorbent size	100 – 160 μm
Bed voidage	0.98 – 0.999

Table 5.8: Design criteria and operating condition of the Zn/Ti sorbent regenerator

Operating conditions	Design criteria
Operating temperature	700 – 750 °C
Operating pressure	19 bar
Gas velocity	6 – 8 m/s
Bed voidage	0.75 – 0.85

5.1.8. Ultra cleaning section

The ultra cleaning section consists of three different units, namely 'Ultra desulphurizer', NH_3/HCl scrubber and 'Active coal filter bed', where unwanted substances are removed to satisfy the product specification.

The ultra cleaning section is based on the two-stage gas-polishing technology [31] where sulfur components and hydrochloric acid will be removed. The two-stage gas-polishing technology can be operated in three different modes, namely:

- The base case where two sorbent columns are used
- Ultra clean with syngas drying where the water is condensed away between sorbent stages
- Ultra clean with HCl scrubber where the HCl and NH_3 is removed using a scrubber between sorbent stages (this mode does not use HCl sorbent).

The article [31] gives the conclusion that if water has to be removed from the gas stream, the ultra clean with HCl scrubber option is the better option, also economically.

The original winning case chain does not include a scrubber option. But the use of sorbent alone leads to enormous amount of sorbent wastes [31]. Further more, the product specification necessitates further reduction of ammonia level and the water vapour in the gas stream must also be removed. Heat integration, which will be discussed in Chapter 5.3, makes it necessary to cool down the gas temperature to approximately room temperature before compression to 40 bars. .

After the first stage desulphurizer the gas stream is sent to the scrubber where the temperature will be lowered to approximately 25 °C that the water in the gas stream will be condensed away. The temperature level of the scrubber fits the heat integration concept. Scrubber application can also solve the ammonia problem. The only negative consequence of using a scrubber is the large amount of aqueous waste. Unlike the solid wastes that have to be disposed of, the aqueous waste problem can be remedied by utilizing a wastewater treatment unit. These aspects show that the application of a scrubber can be justified.

Since the temperature level out of the scrubber is low, it is necessary to operate the second ultra removal stage at low temperature. The use of sorbent is because of this out of the question. The utilization of active coal becomes ideal since it is preferably used at 40 °C [39]. There is no regeneration method for the spent active coal [39]. Therefore the spent active coal will be fed to the gasifier instead of being disposed of as hazardous waste. This must be diluted in the feed stream to avoid problematic feeding due to the viscosity and stickiness of the spent active coal.

Summarizing the ultra cleaning section, the ultra desulphurizer, will push the sulphur component level down to approximately 1 ppmV. The sorbent use in this stage is the same zinc titanate that can also be regenerated in the regeneration section of the bulk desulphurization. The scrubber can bring the HCl and NH_3 level down to respectively < 10 ppbV and < 1 ppmV [31]. The active coal filter unit can remove 99% of HCl and H_2S that the syngas specification can be reached [39]. The active coal filter will also effectively remove the remaining tars in the syngas stream [39].

The first stage ultra cleaning, the ultra desulphurization is applied using a candle or barrier filter reactor. The sorbent is introduced into the gas stream where sulphidation reaction takes place in the candle filter vessel while simultaneously separating the sorbent

from the desulphurized gas stream. The operating condition and design criteria of the ultra desulphurization are summarized in Table 5.9.

Table 5.9: Design criteria and operating condition of the ultra desulphurizer

Operating conditions	Design criteria
Operating temperature	480 – 520 °C
Operating pressure	21 bar
Volumetric gas flow	159 m³/s
Gas residence time	± 5 s
Sorbent type	Zinc titanate
Sorbent size	± 20 μm
Filter face velocity	0.01 – 0.06 m/s
Particulate loading	< 10000 ppm
Backpulse system pressure	Up to 56 bar
Backpulse duration	Up to 1 s
Pressure drop	Up to 1 bar

The tasks bound to the aqueous scrubber, which is commonly a tray absorption column, are the removal of HCl and NH_3. The key component in the scrubber is HCl; larger quantity HCl should be removed with respect to NH_3. Therefore the column is designed to remove HCl to reach the specification of the product. This will determine the dimension of the scrubber. The operating condition and design criteria of the scrubber are summarized in Table 5.10.

Table 5.10: Design criteria and operating condition of the scrubber

Operating conditions	Design criteria
Operating temperature	25 °C
Operating pressure	20.4 bar
Volumetric gas flow	55 m³/s
Exit HCl concentration	1ppbV
Pressure drop	Up to 1 bar

The active coal filter is applied as a guard bed where it can remove small concentrations of harmful contaminants, such as HCl, H_2S and other possible contaminants like mercury [39]. The presence of tars (BTX) will severely limit the capacity to remove other components and moreover might lead to an undesired increase in the pressure drop over the filter. Since the concentration of tars coming in the filter is very low, the presence of tars will not limit the performance of the active coal filter and will be also removed simultaneously. The operating condition and design criteria of the active coal filter are summarized in Table 5.11.

Table 5.11: Design criteria and operating condition of the active coal filter

Operating conditions and efficiency	Design criteria
Operating temperature	40 – 60 °C
Operating pressure	20 bar
Dust content	< 100 mg/m^3
Tars content	< 100 mg/m^3
BTX tars removal efficiency	95 %
Light tars removal efficiency	99 %
Heavy tars removal efficiency	99 %
HCl removal efficiency	99 %
H$_2$S removal efficiency	99 %
Emission metal removal efficiency	99 %

5.1.9. CO$_2$-selective membrane

Several membrane types for CO$_2$ capture systems are available; organic (polymer) and inorganic (ceramic or metallic). Organic membranes are thin layers of glassy polymers, usually an asymmetric membrane that is supported by a porous layer of material without separation properties like composite. Inorganic membranes are chemically stable and pressure resistant. There are two kinds available, porous (ceramic membranes) and non-porous (metallic membranes).

The transport through organic and inorganic membranes undergoes different mechanisms, solution-dilution [43] and configurational diffusion mechanisms ([40][41][42]) respectively. The purpose using a membrane is to remove CO$_2$ from the produced syngas. With a CO$_2$ selective polymer membrane, CO$_2$ permeates through the polymer membrane faster than other component due to its high permeability. On the other hand, gas mixture transport through a ceramic of metallic membrane due to its molecule size towards the pore size of the membrane. Since the molecule diameters of H$_2$ (2.89Å) < CO$_2$ (3.3Å) < CO (3.6Å) [44], it is not possible to remove CO$_2$ without separating H$_2$ and CO using one ceramic of metallic membrane. Therefore, a polymeric membrane is left as the only option to remove CO$_2$ from the produced syngas.

The membrane must be able to operate at 40 bar and 227 ºC. A polymeric membrane is usually not resistant to high pressure and temperature [45]. Other problem is not every polymer membrane is highly selective to only CO$_2$ in a synthesis gas composition. The choice of polymer membrane is therefore limited [46]. Only fluorinated acrylate urethane polydimethylsiloxane (PDMS) membrane as shown in Figure 5.2, a rubbery polymer, is highly selective to CO$_2$ ([46][47]). This membrane has an operation range above its glass transition temperature (-125 ºC) up to 100 ºC [48] and is also high pressure resistant. However, it is not possible to operate at 227 ºC. Therefore, the raw synthesis gas after the compression to 40bar must be cooled at about 95 ºC and using heat integration the clean synthesis gas is heated to 227 ºC. A normal pressure drop of 0.5 bar for membrane operation is used as assumption since no data for the pressure drop over this membrane is available.

$R_A = (CH_2)_3 \, O \, CO \, NH$

$NH \, CO \, O \, (CH_2)_2 \, O \, CO \, CH=CH_2$

$(R_A = \text{urethane acrylate})$
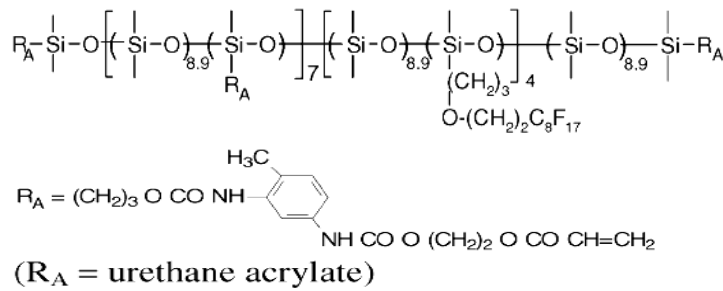
Figure 5.2: Polymer structure of fluorinated acrylate urethane PDMS membrane [47]

As matter of fact, it is very difficult to find permeability data reported for CO_2 removal from a synthesis gas mixture with the chosen membrane at the desired process conditions. A permeability data of normal PDMS membrane for CO_2 removal from a synthesis gas mixture [46] is estimated in combination with the permeability data of PDMS membrane for CO_2 removal from natural gas (CH_4), since it can be assumed that the permeability of CH_4 is approximately twice as big as the permeability of CO and H_2. The reported and estimated permeability data is summarized in Table 5.12.

Table 5.12: Reported and assumed permeability data

Component	Permeability [barrers][5]		
	Normal PDMS	*Fluorinated PDMS*	*Estimated*
CO_2	3200	577	577
CO	400	-	11.5
H_2	500	-	14.4
CH_4	940	27	-

The operating condition and design criteria of the membrane are summarized in Table 5.13.

Table 5.13: Design criteria and operating condition of the membrane

Operating conditions	Design criteria
Operating temperature	< 100 °C
Operating pressure	40 bar
CO_2 removal efficiency	93 %
Pressure drop	0.5 bar

5.2. Support units

The following units will be described in short. They are the supporting units for the biomass gasification plant and are outside the design boundaries, however the fall within our battery limits. In the design, they are considered as a "black box".

5.2.1. Air separation plant [49]

There are in practice three different options for an air separation plant; a cryogenic, a membrane separation and a pressure swing adsorption plant. For the larger quantities of oxygen required for this process, the economically most attractive option is cryogenic distillation.

---

[5] 2.99 barrers = 10^{-15} mol.m.$(m^2Pa.s)^{-1}$

Air Separation in cryogenic distillation begins when air from the atmosphere is compressed to about 10 atm. Hydrocarbons, Water, and carbon dioxide that could freeze later in the process are removed from the compressed air through molecular sieves in the temperature swing adsorber bed. Compressed, dry air is cooled to cryogenic temperatures (about 100 K) by cold process fluids in a series of linear heat exchangers. Compressed, cold air is separated into a bottoms oxygen rich stream and top nitrogen stream in the distillation tower. The oxygen-rich waste stream is flashed through a valve to cool it further and then is used to condense nitrogen coming off the top of the column. The oxygen-rich waste stream is then used to cool incoming air. The waste stream is expanded through a turbine, generating electricity to run the compressor. After being used again to cool incoming air, the expanded waste is either purged to the atmosphere or used to regenerate the adsorber bed. Nitrogen is taken out of the distillation column and partially condensed. The liquid flow back into the column and the vapour is drawn off at the top. This cold nitrogen is used to cool incoming air before exiting the process. However, the nitrogen will not be sold since there is not a big market for nitrogen. A cryogenic air separation plant is expensive and large; the distillation column is several stories high and must be well insulated

5.2.2. Claus unit [25]

Environmental regulations prohibit the amount of sulphur to be disposed into the air. For this reason, a Claus plant has to be installed. The Claus process converts H_2S and SO_2 into elemental sulphur, a product that can be sold. In this design, the SO_2-rich stream coming from the sorbent regeneration process is first partly reduced to H_2S with a small stream of produced syngas. Then the remaining H_2S reacts with the formed SO_2 into sulphur:

$$2H_2S + SO_2 \rightleftarrows \tfrac{3}{2} S_2 + 2H_2O \qquad\qquad \Delta H_{298} = \text{-147 kJ/mol} \qquad\qquad (5.1)$$

Sulphur recovery is limited by the equilibrium. To increase the conversion, the reaction takes place in two or three catalytic converters, placed in series, which operate at 400-500 K. After each reactor, sulphur is removed by condensation. Due to the stringent regulations, the amount of sulphur components in the tail gas from a Claus plant is still unacceptable. However, recent developments (improvements to the Claus process, such as the SCOT or the SuperClaus) have resulted in sulphur recoveries of nearly 100%.

5.2.3. Wastewater treatment

The wastewater in this process will mainly contain traces of ammonia, HCl and possibly salts, since the largest wastewater stream comes from the water scrubber. The ammonia and the HCl leave the wastewater plant as salts. The wastewater is evaporated using LP steam coming from the steam turbine, and recycled in the process. The salts can be used as salt for defrosting roads or as pre-treatment in the metal industry.

5.3. Heat integration

For heat integration of the process in Rotterdam, the pinch technology is used. With this technology usually a pinch, a thermodynamic break in the system, occurs between the hot streams and cold streams. The streams that should be heated (cold streams) or cooled (hot

streams) within the battery limit of the process in Rotterdam (including plant unit, 200 - 600) are given in Appendix 5.2. It is assumed that the heat of the syngas cooler (E201) is totally used to generate electricity. Therefore the heat of this stream is left out of the pinch calculation. The temperature difference between the hot and cold stream is 10°C
By plotting the hot streams and the cold streams in a cascade (see Figure A.5.2.1 in Appendix 5.2), the pinch temperature is calculated at 773K. Because all the heat exchanging streams are below the pinch temperature they can be combined unless:

$$FC_{p,hot} \geq FC_{p,cold} \tag{5.2}$$

$$N_{hot} \geq N_{cold} \tag{5.3}$$

By splitting hot stream <221>-<226> the specifications are met. In Table 5.14 a possible heat integration structure is summarized.

Table 5.14 A summary of the heat integration structure

	E202A	E202B	E202C	E203	E301	E401
Hot stream	<222>-<226>	<222>-<226>	<222>-<226>	<231>-<232>	<302>-<303>	<403>-<405>
FCp hot [kW/K]	286	1120	997	1569	4348	2878
H hot [kW]	135871	532082	473648	54900	995700	218700
Cold stream	<202>-<203>	<210>-<211>	<234>-<235>	-	<401>-<402>	-
FCp cold [kW/K]	285	72	995	-	2878	-
H cold [kW]	-82500	-20930	-131400	-	-218700	-
H rest of hot stream [kW]	53371	511152	342248	54900	777000	218700

It can be concluded that lot of extra cooling utilities are needed to remove the remaining heat of all heat exchangers.

5.4. Process flow scheme (PFS)

In this section, the basic of design will be reviewed step-by-step, along with the Process Flow Scheme (PFS). The PFS, which represents the line-up of the various equipments of the selected process and their connection with the process streams, can be found in Appendix 5.3 The PFS is divided into six plant units; the pre-treatment in the Baltic States, the gasification of wood pellets to clean syngas, the electricity plant, the wastewater treatment, the air separation plant and the Claus plant. Since the focus of the design lies in the supply chain from wood residues to syngas, only the pre-treatment in the Baltic States and the gasification of wood pellets to clean syngas will be explained in details and the other plant unit will be explained briefly.
In the Baltic States, the wood residues <101> are chipped to reduce the size the logs or branches. Some wood residues <103> are lost from the wood chipper (A101). The chipped wood <102> is then compressed using a pelletiser (X101). After this pre-treatment, the wood pellets are transported to Rotterdam Harbour area.
The wood pellets will be stored in the warehouse. A two-days storage column is used for feeding the gasification of wood pellets to clean syngas. From this stored column, the wood pellets feed <201> are pressurized using the recycle stream of syngas in the lock hopper (V201), and fed to the circulating fluidized bed (CFB) reactor (R201). Oxygen <204> is fed to this CFB reactor to provide the heat input by the combustion of the wood pellets in order to bring to the desired operating temperature, and the oxygen source for

the gasification process, which is partial oxidation reaction. The oxygen from the air separation plant <503> is first compressed (K201) before oxygen feed <204> enters the CFB reactor. The steam from the SMDS plant <202> is heated before this steam flow <203> is fed into the CFB in order to inhibit the tars formation and the coking in the CFB reactor. In this CFB, the reactions take place as described in section 5.1.2. The bottom ash <205> is transported out the CFB by using screw transporter (X201).

The product gas from the CFB <206> is filtered with candle filter (S201) to remove ash, dust and solids from the product gas <207>. The filtered product gas <208> is then fed to the monolith tar cracker (R202). In order to achieve the desired operating temperature, oxygen feed <209> is introduced to provide the heat input by combustion of a part of product gas>. First, oxygen from the air separation plant <504> is pressurized by using compressor (K202). Steam from the SMDS plant <210> is heated and this steam <211> is used for cracking the tars and other light alkanes in the product gas. The outlet gas of the tar cracker <212> contains almost no tars and light alkanes and is cooled by using syngas cooler, a high shell-tubes heat exchangers column. The heat is removed by using process water from the electricity plant <304>. The produced steam <301> is used to generate the electricity using a turbine <T301> in the electricity plant.

Afterwards the cooled gas is compressed (K203) and this pressurized gas <214> is fed to the Sour water-gas shift reactor (R203). For the water-gas shift, water feed <216> is fed to this reactor, where the process water <215> is first pressurized by using a pump (P201).

The product gas with desired H_2/CO ratio <217> is then cleaned with hot gas cleaning system. First the large part of the sulphur compounds, like H_2S and COS is reduced by the Zn/Ti sorbent in the Bulk desulphurizer (R204). The purified gas <218> is sent to the Ultra desulphurizer (R206) to remove the remaining sulphur compounds to 1 ppmV. The spent sorbent from both desulphurizer (<219> and <222>) is regenerated in the Zn/Ti sorbent regenerator (R205). Some spent Zn/Ti sorbent <240> is purged, since it becomes dust and cannot be recycled to both desulphurizers. The sour gas from the regeneration <225> is sent to the Claus plant. Some make up Zn/Ti sorbent for the Bulk desulphurizer <238> and Ultra desulphurizer <239> is added to the sorbent streams to both desulphurizers, <220> and <223> respectively. The purified gas <218> and the Zn/Ti sorbent stream <223> are mixed in mix hopper (V202) and the removal of remaining sulphur compounds take place in the ultra desulphurizer (R206), which also acts like the candle filter to separate the sorbent fro m the purified gas <221>.

Before entering the NH_3/HCl scrubber (C201), this gas is cooled by using combined heat exchanger (E202 a, b, c). The NH_3 and HCl in the cooled gas <226> is adsorbed with water stream <228>. The process water <227> is pressurized by using pomp (P202) before entering the scrubber (C201). The wastewater <230> is then sent to the wastewater treatment. When the measured chlorine level in the gas streams <217> exceeds the design criteria of the scrubber, the active coal filter bed (C202) will be used.

This purified gas <229> is then pressurized by using compressor (K204) and cooled with cooling water (E203). To achieve 5% inert in the syngas, the produced CO_2 <233> during the process is removed by using CO_2 selective membrane (S202). The desired syngas with 5% inert <234> is obtained and it must be heated (E234) to accomplish the required specification. This stream will be split into two streams, where one is sent to the SMDS plant <237> and the other one to Claus plant <236> to reduce SO_2 to H_2S.

As mentioned above, the produced steam <301> from the syngas cooled (E201) is sent to steam turbine (TG301), where electricity is generated. This electricity will be used to fulfil the power for compressors in the gasification of wood pellets to clean syngas. The steam out the turbine <302> is used to evaporate the wastewater stream <401> and to remove the salts <404>. Some water <407> is purged and large part of this salt-free water is recycle as process water <406>. The hot water <303> from the evaporator (E301) is pressurized using pump (P301). This pressurized water <304> is recycled to the syngas cooler (E201) to produce high-pressure steam for the steam turbine (TG301).

Air <501> is distillate cryogenically to produce oxygen (<503> and <504>) for the gasification of wood pellets to clean syngas. Produced nitrogen <505> is purged to the atmosphere since the market of nitrogen is too small for purchasing this nitrogen.

Some syngas <236> is sent to Claus plant for reducing the sour gas <225> to H_2S. Sulphur <601> is produced from this Claus plant and sold as by-products. The waste air <602>, which is free from S-compounds, can be then purged to the atmosphere.

5.5. Process stream summary

The process stream summary of the whole process (100 till 600) is given in Appendix 5.4. In Chapter 7 the mass and heat balances are checked for consistency.

5.6. Utilities

In Appendix 5.5 the Utility Summary is given. It shows that 168577 ton cooling water per hour is needed. Also per hour 708133 kWh electricity is needed to drive the defined compressors and pumps in the process, in spite that the turbine produces 270100 kWh/h of electricity. Heating equipment is not necessary.

Cooling takes only place with cooling water, since the streams need not to be further cooled than 25 °C (so no cooling refrigerant is needed) and the flow rate of the streams that are cooled are large (so cooling with oxygen should take place in very large heat exchangers).

The major use of cooling water is for decreasing the temperature of the syngas stream from the gasification temperature of 900 °C till 25 °C before the NH3/HCl scrubber. This use can hardly be reduced since the low temperature of 25 °C should be reached for condensing water in the syngas stream and the membrane operates at maximum 95 °C. Within the process in Rotterdam there are few streams that should be heated up in the plant relatively to the numbers of streams that should be cooled. Therefore it is difficult to reduce the amount of cooling water needed. A possible solution could be synergy with other plant at the Maasvlakte. Also low temperature input streams can be heated more than is done by the heat integration study in this design, like pure oxygen (<503> and <504>).

Electricity is mainly used by the compressors for pressurizing the syngas stream from 7 to 40 bar. This quantity also can hardly be reduced. It should be avoided to use intercoolers for the compressors; this reduces the energy efficiency of the compressor. A decrease in the electricity consumption can not easy obtained, on the other hand the production of electricity can be increased through more extensive heat integration for generating valuable steam. It should also be noted that not all steam of the SMDS plant is used in the gasification process. This steam can also be used to generate electricity.

5.7. Process yield

In Figure 5.3 the Process Yield of the flows passing the battery limits is graphically represented. In Appendix 5.6 the more information can be found.
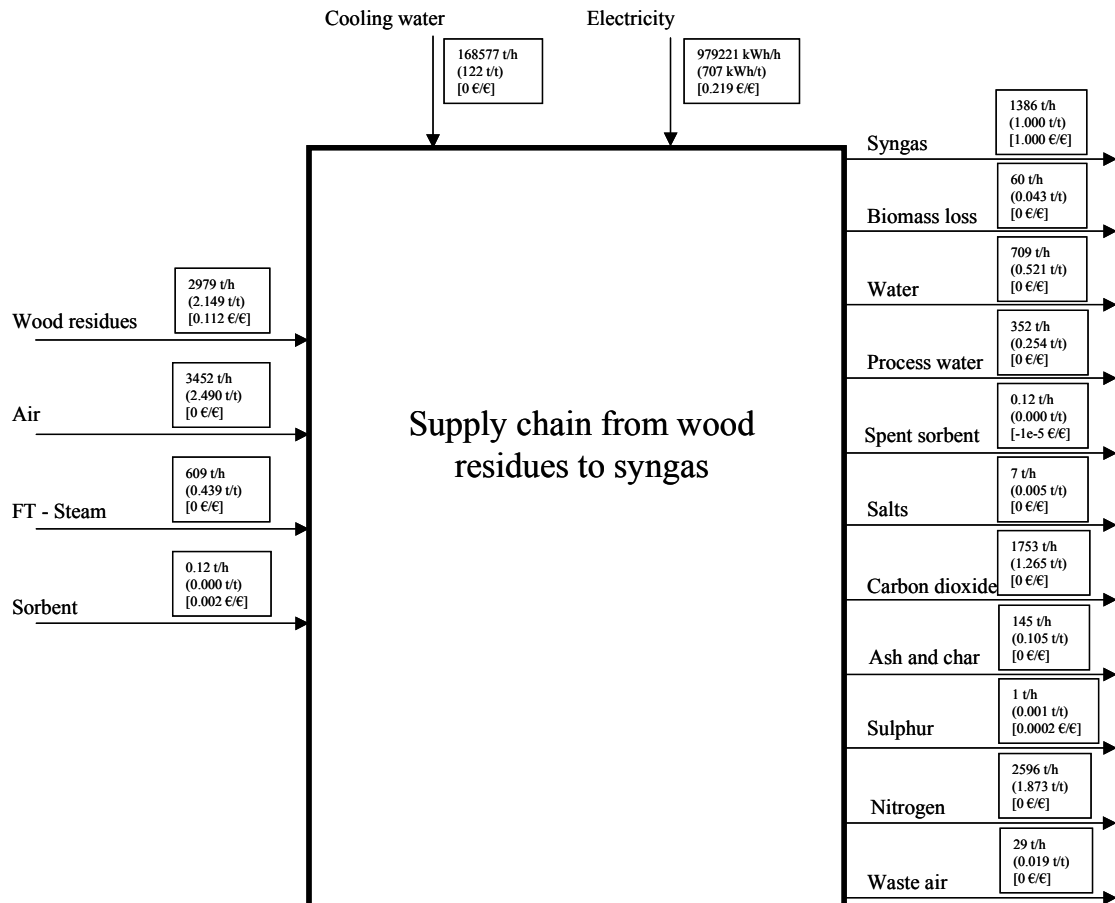

Figure 5.3: Process Yields

Besides the flows given in Figure 5.3, there are also streams, which will pass the battery limit, once in a time. These streams are: the monolith of the tar cracker (1x in 5 years), the catalyst for the SWGS reactor (CoMoS) (1x in 5 years), the catalyst for the Claus plant (alumina) (1x in 5 years) and active coal (10 ton per year).

6. Process control

In this chapter the defined goal of the process control structure as well as the performed procedure behind the process control structure, will be explained and discussed.

6.1. Control objectives

A chemical plant must satisfy several requirements, which can be achieved using a process control structure. The main requirement is a safe process, to guarantee the well being of the people in the plant, the people outside the plant and to maintain an economic development. Another important requirement is the product specifications required by the clients. These specifications are given in Chapter 3. The third requirement is that the plant is operated within environmental regulations. These regulations comprise for instance emissions of CO_2 and SO_2 or the quality of the water returned to a river or lake. The fourth requirement is the operational constraints and these are constraints inherent to the operation of certain equipment. For instance the temperature in the catalytic cracker should stay within certain limits. The last requirement is the economics, which means that the plant should be operated at given optimum levels of minimum operating costs, maximum profit, etc.

Concluding, the process is controlled on five different aspects in order of priority:

1. Safety
2. Product specifications
3. Environmental regulations
4. Operational constraints
5. Economics

Luyben [50] gives a philosophy in designing a process control structure, which states *"It is always best to utilize the simplest control structure that will achieve the desired objective"*. Some guidelines for designing a process control structure are applied [50], such as Luyben's law.

Using the analysis of the HAZOP study, the control structure is designed, since in the HAZOP study possible hazards and difficulties in the operability are identified. The proposed control structure of the design can be found in the Process Flow Scheme in Appendix 5.3.

6.2. Proposed Control structure

The proposed control structure will be explained step by step for the major equipments and in general for supplementary equipments like, pumps and compressors.

6.2.1. Circulated Fluidised Bed reactor (CFB) (R201)

The CFB is the hart of the process and has many variables that have to be controlled. The first variable is the pressure in the lock hopper (V201). The lock hopper is used to pressurise the wood pellets and the pressure has to be high enough to enter the CFB. A pressure-controlled valve is placed on the syngas recycle, which will act on the pressure in the lock hopper. The second variable is the screw that transports the pellets into the

TUDelft

CFB. In case of a failure to this screw, the wood pellets stream <201>to the lock hopper will be first closed and other input streams to CFB and tar cracker will also be shut down since emergency alarm will closed all valves to CFB and tar cracker. Since ten CFB's and ten monolith tar crackers are installed, it is not necessary to shutdown the rest of the process when this screw is failed. The third variable is the outlet temperature of the CFB, which determines the composition of the product gas <206>. To obtain a constant composition a temperature controller is placed on the oxygen feed stream <204> and is controlled by the outlet temperature in the riser of the CFB. Since oxygen and steam are coupled by a specific ratio, a ratio controller is placed between both streams to ensure a constant ratio between steam and oxygen. The fourth variable is the ash in the CFB. This is removed with a transport screw to an intermediate chamber, cooled and with a second screw (X201) transported outside <205>. The intermediate chamber has a minimum required fill to prevent any product gas escaping with the ash. A level controller placed in the intermediate chamber controls the second screw.

6.2.2. Candle filter (S201)

The candle filter is used to remove the fine particles from the gas stream. A pulse gas is used to periodically remove the ashes from the filter. The variable in this system is the pressure drop. A pressure controller is used to keep the pressure drop within acceptable limits.

6.2.3. Monolith tar cracker (R202)

The monolith tar cracker is used to convert tar to carbon monoxide and hydrogen and to convert methane to syngas. So it is important to completely remove the tar, because the condensed tar can cause plugging in the syngas cooler. The pressure and temperature of the outlet stream <212> are good indication on the concentration of tars.

The main objective is to completely convert all tar in the product gas to syngas. When more tars are present in the feed <208>, the temperature will decrease, which affects the tar cracking reactions. More oxygen <209> is needed for the combustion to provide the heat and steam can remain constant, because of the surplus already present.

When the feed contains less tar, the temperature will increase due to less energy consumed by the tar cracking reactions. To keep the temperature within limits more steam <211> is added. This can be explained by the fact that light alkanes will not be cracked when oxygen feed <209> is reduced.

A temperature controller at the end of the reactor sends information to a high selector (HS) and a low selector (LS). The high selector sends information to a flow controller on the steam input <211>. The low selector sends information to a flow controller on the oxygen input. These selectors will control the temperature by adjusting the flow of steam or oxygen without interfering each other.

A second variable of the monolith tar cracker is the pressure drop over the monolith. A pressure difference transmitter is used to monitor the state of the monolith. An increase of pressure drop means blockage or plugging of the monolith and maintenance has to be performed.

6.2.4. Syngas cooler (E203)

The syngas cooler is controlled with a flow controller on the cold stream inlet, process water <301> and obtains information from a temperature transmitter on the hot stream outlet, the cooled gas <213>. This ensures the right temperature of the syngas stream <213> before entering the compressor.

6.2.5. Sour water-gas shift reactor (SWGS) (R203)

The sour water-gas shift is an important reactor of the whole system, since this reactor controls the specifications of the syngas stream, the H_2/CO ratio. Information needed is the composition of the feed stream <213> and the temperature. The problem is the time delay due to the composition measurement. Therefore the pressure and temperature of the stream leaving the monolith tar cracker <212> are measured. With this information the equilibrium composition can be calculated which, combined with the temperature of the feed <214> to the SWGS, results in specific water feed <216>. The water stream is controlled by this information. Here, a specific computer will be needed to calculate online the required specific water stream <216> from the temperature and equilibrium composition data.

6.2.6. Bulk desulphurizer (R204), Ultra desulphurizer (R205), and Zn/Ti regenerator (R206)

The first step in the gas cleaning is the bulk desulphurizer (R204). In this reactor the major fraction of sulphur compounds is bounded to ZnO as is described in Chapter 5. It is important that a continuous stream of fresh sorbent enters the reactor (<238> and <239>). However to prevent overloading of the reactor the make up sorbent is controlled with a flow controller. Information about the flow of sorbent leaving the reactor <240> is send to a ratio controller. A ratio controller is needed because the bulk desulphurizer (R204) and the ultra desulphurizer (R206) both need fresh sorbent. The make up stream for the ultra desulphurizer is also controlled with this ratio controller.

The risk calculation analysis by F&EI has shown a significant degree of hazards in the Zn/Ti regenerator (R205) for the sorbent. In this column a highly exothermic reaction takes place combined with fine particles and an oxidizing environment leads to possible runaways or even dust explosions. It is important that the sorbent cannot accumulate in this reactor. Therefore the flow leaving the bulk desulphurizer <219> and Ultra desulphurizer <222> adjusts the amount of sorbent from R204 and R206 to the Zn/Ti regenerator (R205). A temperature controller is installed to adjust the air stream <224> in case of a temperature increase or to close the valve when the temperature has tendency to increase rapidly. Since it is difficult to control the pressure in this regenerator to avoid the dust explosion, a bursting disk is installed as recommended from the analysis of HAZOP study.

To prevent plugging of the ultra desulphurizer a similar control structure as the candle filter is used.

6.2.7. NH₃/HCl scrubber (C201)

The NH_3/HCl scrubber (C201) is used to remove the chlorine and ammonia from the syngas. The scrubber is a rather safe device and a level transmitter is used to make sure

that the scrubber will not get flooded. The process water <228> is fed to scrubber in specific ratio with the absorption factor. Therefore the gas flow <226> to the scrubber is measured and used to control the flow of process water with a ratio controller.

6.2.8. Active coal filter bed (ACF) (C202)

The active coal filter is a safe guard device, which is used only in case of problems upstream or with the feed. This means that every shipment is checked and when too many impurities are in the feed the valve to the active coal filter is opened and the stream to the compressor will be closed. Problems upstream can be an undesired low flow to the absorber or a malfunction in the bulk desulphurizer.

To ensure a required activity of the coal filter, a pressure difference transmitter is used to indicate the amount of impurities absorbed on the active coal

6.2.9. CO_2-selective Membrane (S202)

The membrane is used to separate carbon dioxide from the syngas stream. The membrane is a very simple device and is only monitored for blockage or broken parts with a pressure difference transmitter, since it consists of thousands of hollow fibres.

6.2.10. Pumps and compressors

The pumps are all controlled with a standard flow controller after the pump to prevent that the pump runs dry. The compressors are all controlled with a pressure controller that adjusts the electricity to the compressor.

7. Mass and Heat Balances

7.1. Balance for Total Streams per equipment

In Table A.7.1 Mass and Heat balances (total streams) are given for all the equipments in different plant units (from 100 till 600). Data consistency is reached, since per equipment the total streams of mass and heat of the input are largely consistent with the total streams of the output. There are some little imperfections, around the bulk desulphurizer (R204) and the ultra desulphurizer (R206). This is due to the fact that the modelling of the desulphurizers is partly done by ASPEN and the other part by hand-calculations. This imperfection does not influence the final results of the process stream summary, since the gas streams, which are the important ones, are precisely modelled with ASPEN and the solid streams of sorbent are added afterwards.

From the mass and heat balances of the total streams, the heat input and output, which is not accompanied with a certain mass flow, can be calculated, see Table A.7.2. These are for example the heat removed by cooling, or the heat added by compressing. The heat input/output values are used for heat integration calculations (see section 5.3) and utility determination (see section 5.6).

7.2. Balance for Stream Components around the battery limit

The mass and heat balance per component around the overall battery limit is also given in Table A.7.3. The difference between the mass input and output is almost zero and therefore acceptable. The difference between the heat 'in' and 'out' is -1500 MW. This value is comparable with the value given in Table A.7.2 in Appendix 7 (heat input and output, which is not accompanied with a certain mass flow). Therefore it can be stated that also the heat balance around the battery limit is consistent.

TUDelft

8. Process and Equipment Design

In this chapter the process integration using an ASPEN model is discussed. Further, the design of each of the main equipment is explained. And finally a summary of the equipment design is tabulated at the end of the chapter. The model is given in Appendix 8.1.

8.1. Integration by process simulation

ASPEN PLUS 11.1 is used to model the gasification process and the gas cleaning train. During this phase several problems were encountered. To overcome these problems different assumptions are made and these are described in the following paragraphs.

8.1.1. Circulating Fluidized Bed reactor (R201)

The CFB is very difficult to model in ASPEN. The kinetics of wood gasification is not known (see Chapter 4.2) therefore it is impossible to use a kinetic model in ASPEN. The gasification is modelled with an 'Ryield' reactor. In this reactor the outcome is specified based on the mass going into the reactor. The outcome of the reactor is copied from data found in literature [5]. In ASPEN the solids are left out of the process since their influence on the entire flow sheet is limited. Another consideration to leave them out is that solids, that are user defined in ASPEN, can cause a lot of problems, although in this case they act as an inert.

8.1.2. Monolith tar cracker (R202)

In the tar cracker alkanes are partly burned for the heat input and tar is cracked with steam and carbon dioxide, which consumes this energy (see Chapter 4.3). To better understand what happens these two mechanisms are separated. In the first reactor the alkanes are burned with oxygen and in the second reactor the cracking reactions (Chapter 4.3) take place and steam is added for a better cracking yield. The process is fine tuned on the temperature leaving the second reactor, which has to be 900 $^{\circ}$C. This can be achieved by adjusting the oxygen input in the first reactor.

The first reactor is an 'RStoich' reactor and for the two combustion reactions a fifty-fifty conversion of methane and ethane is assumed. The second reactor is an 'RGibbs' reactor in which by a Gibbs minimization the equilibrium composition is calculated. This specific reactor is chosen due to a lack of reliable and well-described catalytic tar cracking kinetics. Two assumptions are made, the first being that at these high temperatures the equilibrium is reached and the second is that the equilibrium is limited to tar, hydrogen, steam, carbon monoxide and carbon dioxide.

When this method is chosen it is important to make sure that all oxygen entering the first reaction is consumed, because otherwise it interferes with the equilibrium reactions in the second reactor, thus making the distinction between the two mechanisms disappear.

8.1.3. Sour water gas shift reactor (R203)

The sour water gas shift reactor is operated at 500 $^{\circ}$C and at these temperatures the reactions taking place (Chapter 4.4) reach their equilibrium state in short residence times (seconds). The reactions taking place are all equilibrium reactions and therefore the

TUDelft

'RGibbs' reactor is used to model these reactions. Another reason was the lack of detailed kinetic values for all reactions. Pressurized water is pumped into the SWGS to get the right equilibrium composition and to cool the slightly exothermic reactions that take place.

8.1.4. Bulk desulphurizer (R204) and ultra desulphurizer (R206)

The sulphidation reaction for the desulphurizers is well described in literature [28][29] and can be entered in ASPEN. The real problem in ASPEN is the residence time difference of the solids and the gas. The gas phase has a shorter residence time than the sorbent. The second problem is the activity of the catalyst, which cannot be modelled in ASPEN. The gas phase residence time is chosen as the characteristic residence time and an overall activity is assumed. These same problems exist in the ultra desulphurizer and are solved the same way.

The bulk desulphurizer is a transport reactor, in which the gas phase behaves as a plug and overall a plug flow exists. The 'RPlug' describes this behaviour best. The ultra desulphurizer is a barrier reactor, in which the gas phase is mixed. The 'RCSTR' describes this behaviour best.

8.1.5. Zn/Ti sorbent regenerator (R205)

The kinetics of the regenerator is known [32]. This kinetics is modelled in ASPEN in an 'RPlug' reactor. The problem here is the other way around compared with the desulphurizers. So in this model the residence time of the sorbent is chosen as well as an overall activity. An 'RPlug' reactor describes best the hydrodynamics of the reaction.

8.1.6. NH$_3$/HCl scrubber (C201)

The scrubber was first modelled with an electrolyte model. This model is specific for absorption processes. The model is operated at varying flow rates and varying tray numbers. This has no effect on the amount of hydrogen chlorine absorbed, which was expected. Therefore the absorption is modelled in Excel using the Henry coefficients (Chapter 4.7) and the results are translated to ASPEN in a separation unit (SEP2).

8.1.7. CO$_2$-selective membrane (S202)

A membrane is not a standard feature in ASPEN. Therefore a Mathcad file is written (Appendix 8.2) in which the separation of carbon dioxide, combined with a slip of carbon monoxide and hydrogen, is modelled. These values are entered in ASPEN in a separation unit (SEP2), resulting in a purified syngas.

8.1.8. Equipments in ASPEN, which are not modelled

The process modelled in ASPEN mainly concerns section 200, everything that happens in the Baltic States is not modelled with ASPEN. The solids that are formed in the CFB are kept out of the system, to avoid possible problems. This means that the candle filter, used to separate gas and solids, is not modelled. The loop of sorbent from the regenerator is not modelled in ASPEN. The reason is that it is not the main process and there is no added value to our model. The active coal filter is a back up equipment and therefore not taken into account in the ASPEN model.

TUDelft

8.2. Equipment selection and design

Continuing the selection process this chapter will discuss the designs and dimensions of the equipment in more detail. Calculations done in the design process for each unit operation can be found in Appendix 8.2.

8.2.1. Circulating fluidized bed reactor (R201)

An estimate for the volume of the CFB is made with the use of residence times from literature ([5][21][51]). The residence time in a CFB depends on a lot of factors, but an important one is the size of the wood chips. For wood chips smaller than 1 mm, the residence time is several seconds. For particles of a few centimetres up to a decimetre, this can be many minutes. For biomass application in a CFB, the fuel must undergo a size reduction to 25-50 mm [21]. The particles entering the CFB have a dimension of 1×3 cm, resulting in an average residence time of 1 minute.

Due to the high production rate (8000 MW syngas) that has to be reached, the process consists of 10 CFB's, each generating 800 MW of syngas. At present, these very large CFB's do not exist, but it is thought to be feasible within ten years. Atmospheric air-blown gasifiers with a thermal input of 150-200 MW have been operated on a commercial scale. Currently natural gas, oil or coal gasifiers are built in the range from 500-1250 MW$_{th}$ and coal combustors exist up to 1500 MW$_{th}$ [25][52].

The required volume for 1 CFB is estimated using equation 8.1, with an average residence time of 60 seconds and the exit volumetric flow rate of 500 m^3/s.

$$V_{CFB} = \frac{\phi_V}{N_{CFB}} \cdot \tau \qquad\qquad (8.1)$$

where:

V_{CFB}	: Volume of the CFB	[m^3]
ϕ_v	: Volumetric flow rate of the feed	[m^3 s^{-1}]
N_{CFB}	: Number of CFB	[-]
τ	: Residence time	[s]

This results in a single CFB volume of 3100 m^3. The calculation can be seen in Appendix 8.2.

The CFB gasification system consists of a reactor where the gasification takes place, a cyclone to separate the particles from the gas, and a return pipe for returning the particles to the bottom part of the gasifier.
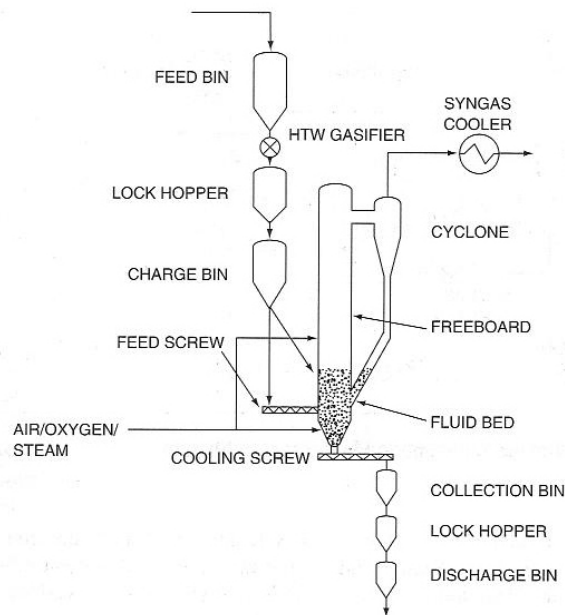
Figure 8.1: Schematic representation of the CFB system.

The oxygen and steam are fed to the bottom of the reactor via a distribution grid. The gas velocity is so high that many particles are conveyed out of the reactor and into the cyclone. Biomass particles are fed directly in or on top of a bed of sand. The sand serves as a heat carrier and stabilizes the temperatures in the process. The ash is removed from the bottom of the gasifier with a water-cooled bottom ash screw.

The bed diameter and height are mainly determined by the feed rate, the amount and velocity of oxygen and steam, the amount of solids circulating, the ratio between gas and solids and the average residence time. Since it is very complicated to calculate a CFB diameter and height, these parameters are estimated with data from experiences from practice [52]. A volume ratio of the riser to downer is assumed to be 2. Further a fixed height to diameter ratio of 6, which is estimated from literature, is used. Using equations 8.2 and 8.3 a height of 45.6 m and a diameter of 7.6 m per CFB can be calculated with a corresponding volume of 3100 m^3, see Appendix 8.2.

$$V_{CFB} = V_{Riser} + V_{Downer} \qquad (8.2)$$

$$V_{Riser} = H_{CFB} \cdot \pi \cdot \left(\frac{D_{CFB}}{2} \right)^2 \qquad (8.3)$$

where:

V_{CFB}	: Volume of the CFB	[m^3]
V_{Riser}	: Volume of the riser	[m^3]
V_{Downer}	: Volume of the downer	[m^3]
D_{CFB}	: Diameter of the CFB	[m]
H_{CFB}	: Height of the CFB	[m]

Material

Temperatures in fluid-bed gasifiers can go up to 1100 ºC, therefore, insulating brick walls are preferred. These walls consist of two layers: a layer of insulating bricks (silica firebrick) to protect the outer steel shell of the reactor from the heat and an inner (hot) layer of more compact bricks (castable bubble alumina) that can withstand the high temperatures. There is mechanical erosion from the ash and the sand. Wall thickness is typically 60-70 cm.

Feeding biomass into a pressurised reactor is done with a lock hopper, followed by a feeding screw. In general, a lock hopper system consists of two or three vessels that are situated on top of each other and are separated by valves. These vessels are pressurised one by one, and in this way, the solid particles are introduced in the feeding screw and then into the pressurised reactor. In the same, but reversed way, the ash leaves the CFB. Syngas is used here as a transport gas to operate the lock hopper. The advantage of using syngas instead of nitrogen as a transport gas is that there is no nitrogen contamination of the syngas. Nitrogen is very difficult to separate from syngas and would form a problem later on in the SMDS process. CO_2 could also be used, but since syngas is already at high pressure, an expensive compression can be saved.

8.2.2. Candle filter (S201)

The filter design calculation is based on the dimension of the barrier filter designed by Westinghouse [54] (Figure 8.2). This vessel is capable of withstanding the pressure and temperature requirements of the process, P = 7 bar and T = 900 °C. The highest candle array density is used, namely 61 candle elements per plenum. A plenum is a part of the candle filter where a set of candles is bundled.
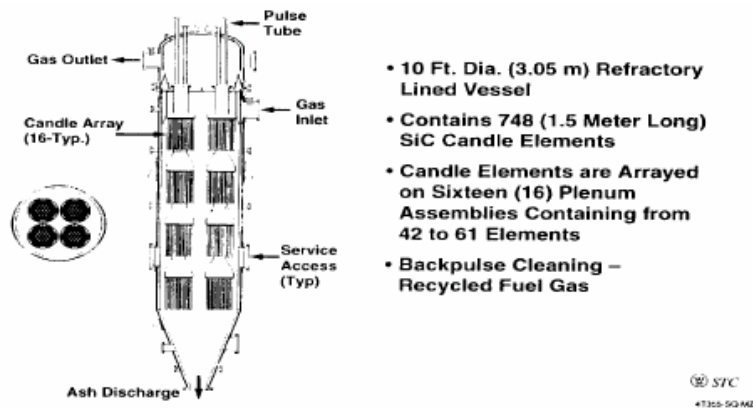
Figure 8.2: Westinghouse barrier filter

Typical the operating face velocity of a candle filter ranges from 0.01 - 0.06 m/s. Scale-up of a candle filter is usually done by increasing the plenum diameter so that more candle elements can be fitted or by increasing the number of plenums. In other words, increasing the dimension of the filter vessel. For the capacity of the process the barrier filter shown in Figure 8.2 is scaled-down to 8 plenums. The total number of candles in the vessel is then 488. The candle has a height of 1.5 m and a candle diameter of 15 cm is assumed.

The relation of the volumetric flow rate (capacity) to the face velocity is:

$$\upsilon_{face} = \frac{\phi_V}{A_{filter}} \qquad\qquad (8.4)$$

where:

υ_{face}	: Face velocity through the candle	[m s^{-1}]
ϕ_v	: Volumetric flowrate of the feed	[m^3 s^{-1}]
A_{filter}	: Total filter area	[m^2]

As base of the calculation a face velocity of 0.04 m/s is assumed. The calculation shows that 1 candle filter of 52.8 m^3 is needed after each CFB, see Appendix 8.2.

Material [54]
The internals of the vessel are designed using a high silicon stainless Alloy, RA85H, to resist metal dusting, a catastrophic form of carburization. The filter unit is designed for Seismic Zone 4 to protect the internals from damage due to lateral displacement in a seismic event.
The vessel is equipped with the commercially available clay bonded silicon carbide (SiC) candle filters. The structure of these elements is mainly a coarse-grained SiC bonded by a clay-based binder. Each element is provided with a fine-grained SiC or aluminosilicate fiber outer skin that serves as the filtration surface. Alternate, oxide-based ceramic materials are also being developed for ceramic barrier filter application.

8.2.3. Monolith tar cracker (R202)

For modelling the tar cracker in process simulation (Chapter 8.1) it is assumed that equilibrium is reached, which is a good approximation (Chapter 4.3). For calculating the sizes of equipment for the monolith tar cracker the kinetics for tar decomposition found in literature [22] for a packed bed are used, since no data is available for a nickel monolith catalyst. The conversion of tar is 99.9%. It is also assumed that 10% of the catalyst in the packed bed is actually used during reactions. With these assumptions, the catalyst in the monolith is estimated and the size of the monolith tar cracker is calculated. In Appendix 8.2 the calculation is given.

Material
At such a high temperature Incoloy, a nickel chromium alloy has to be used [14]. This material has high resistance to carburization and cyclic oxidation.

8.2.4. Syngas cooler (E201)

The design of the syngas cooler is based one some parameters calculated using ASPEN PLUS, e.g. the heat duty, flow of water or steam through the cooler and the heat exchange area. ASPEN gives a required heat exchange area of 6872 m^2.
For the estimation of the dimension, calculations are based on a shell and tube heat exchanger design, as described in Coulson and Richardson's Chemical Engineering - Volume 6 [53]. According to [53], the maximum tube diameter that can be used is 5 cm. However pictures of syngas cooler in gasification plant suggest that a diameter of 10 cm is more realistic. The estimation is done using equations 8.5 and 8.6 and is calculated using MathCAD.

$$N_{tubes} = \frac{A}{A_{tube}} \tag{8.5}$$

$$D = D_{tube} \left(\frac{N_{tubes}}{0.32} \right)^{\frac{1}{2.14}} \tag{8.6}$$

where:

N_{tubes}	: Number of tubes	[-]
A	: Total heat exchange area	[m^2]
A_{tube}	: Tube heat exchange area	[m^2]
D	: Vessel diameter	[m]
D_{tube}	: Tube diameter	[m]

This results in a height of 36.9 m and a diameter of 4.9 m for 1 syngas cooler.
The hot steam is sent from the syngas cooler to a steam turbine, which converts the high-pressure steam into atmospheric steam and electricity. This turbine generates 27 MW per syngas cooler. This result also comes from the flowsheet model in ASPEN PLUS. Steam turbines can operate up to a temperature of 500-650ºC.

Material
Due to the high temperature, stainless steel (alloy) is used as the construction material.

8.2.5. Sour water gas shift reactor (R203)

The Sour-WGS reaction takes place in an adiabatic fixed bed reactor. Since no kinetics is known some simplifications are made. Most calculations are done with simple formulas that were not using kinetics expression. A complete set of the formulas used can be seen in Appendix 8.2. The pressure drop is calculated using the Ergun equation (Eq. 8.7)

$$\frac{-\Delta P}{H_{bed}} = 150 \cdot \frac{\mu \cdot \upsilon}{d^2} \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \cdot \frac{\rho_f \cdot \upsilon^2}{d} \cdot \frac{(1-\varepsilon)}{\varepsilon^3} \tag{8.7}$$

where:

d	: Particle diameter	[m]
H_{bed}	: Bed height	[m]
ΔP	: Pressure drop	[bar]
υ	: Superficial gas velocity	[m s^{-1}]
μ	: Viscosity	[Pa s]
ρ_f	: Gas density	[kg m^{-3}]
ε	: Bed porosity	[-]

To take the process chain into consideration two sour-WGS reactors is assumed. Using a residence time of 1.6 s, a bed porosity of 0.4 and a pressure drop of 4 bars the reactor dimension is calculated, see Appendix 8.2 for the calculation. The calculation results in the following dimensions, namely a reactor diameter of 6.19 m and reactor height of 3.5 m. The volume that belongs to these dimensions is 105.5 m^3.

Material

TUDelft

At a temperature level of 500 °C, stainless steel (alloy) vessel can be applied [14].

8.2.6. Bulk desulphurizer (R204) and Zn/Ti sorbent regenerator (R205)

Bulk desulphurizer
At a gas velocity of 10 m/s the optimal sulphidation rate occurs at a gas residence time of approximately 2 seconds, see Appendix 8.2. This finding is confirmed by the literature [31]. Using this value, the height of the reactor is calculated to be 20 m. By relating the volumetric flow rate to the height of the reactor, the diameter can be calculated. The high raw syngas flow makes it necessary to use 2 reactors as described above to fulfil the desulphurization task. The calculation (see also Appendix 8.2) results in a reactor diameter of 3 m. Due to the behaviour of the transport reactor, which operates in the pneumatic flow regime, the system can be modelled using a plug flow model, also verified in literature [31]. In combination with the kinetics discussed in chapter 4 the desulphurization process can be simulated. The performance of the bulk desulphurization, which is to reduce the level of the sulphur components in the main gas stream down to approximately 20 ppm, can then be tested.

Material
At a temperature level of 500 °C, stainless steel (alloy) vessel can be applied [14].

Zn/Ti sorbent regenerator
Gas velocity of around 6 m/s brings the reactor into entrainment regime. Assuming the same gas residence time of 2 seconds the dimension of the reactor is estimated using the same method for the bulk desulphurizer. This results in a height of 12 m and diameter of 2 m. To simplify the calculation the regenerator is modelled as CSTR to model the well-mixed sorbent bed followed by a plug flow to model the reaction in the freeboard. Regeneration occurs mainly in the mixing zone so further simplification by neglecting the plug flow part can be justified [55]. The calculation can be seen in Appendix 8.2.
The regeneration time for the sorbent is shorter than the sulphidation time [56]. Maintaining a constant sorbent circulation between the desulphurizer and regenerator should not affect the desulphurizing performance of the unit.

Material
The high temperature in the regeneration zone makes it necessary to use high temperature resistant material like Incoloy [14].

8.2.7. Ultra desulphurizer (R206)

Like the candle filter design, the reactor design calculation for the ultra desulphurization is based on the dimension of the barrier filter designed by Westinghouse [54], see Figure 8.2. This vessel is capable of withstanding the pressure and temperature requirements of the process, P = 20 bar and T = 500 °C. The highest candle array density is also used, namely 61 candle elements per plenum.

To serve the capacity of the process the barrier filter shown in Figure 8.2 is scaled-up by adding one more plenum cluster that consists of 4 plenums. The total number of candles in the vessel is 1220.

The dimension of the filter vessel is calculated using the same method used in candle filter design by fixing the face velocity (0.04 m/s). Calculation shows that 4 barrier filter reactors will be needed, see Appendix 8.2. Two barrier filter reactors will be installed in parallel in each of the gas-cleaning trains of the process. The calculated volume of the vessel is 73 m^3 .The filter is cleaned periodically by back-pulsing recycled desulphurized syngas.

Material [54]
The material used for the ultra desulphurization barrier reactor is identical to the candle filter discussed in section 8.2.3.

8.2.8. NH$_3$/HCl scrubber (C201)

The equipment size and pressure drop of the scrubber is calculated using the method, which is described in J.D. Seader and E.J. Henley [34] for designing an absorption column. The key component is HCl, as already stated in Chapter 5. The calculation is given in Appendix 8.2

It is assumed that the tray spacing between the trays is 2 ft (0.61 m) and the absorption factor is optimal at 1.4 [14]:

$$A_{HCl} = \frac{L}{K_{HCl}G} = 1.4 \tag{8.8}$$

where:

A	: Absorption factor	[-]
L	: Liquid flow rate	[m^3 s^{-1}]
G	: Gas flow rate	[m^3 s^{-1}]
K	: Equilibrium constant	[-]

The shortcut design to determine the number of stages is:

$$N + 2 = 6 \cdot \log \frac{y_{HCl,in}}{y_{HCl,out}}$$

Since the liquid (water) flow rate is fixed by the key component, the absorption factors for the other components can be calculated and thus the fraction of that component in the outlet gas stream. The calculation of the efficiency of removal of other components is given in Appendix 8.2.

Material
A carbon steel vessel is sufficient to operate at the scrubber temperature range. The tray is made of stainless steel (SS314)

8.2.9. Active coal filter bed (C202)

Depending on the adsorbent regeneration method, a contacting device can be chosen [34]. There are several contacting devices, like slurry bed in agitated vessel, moving bed,

combined fluidized bed-moving bed and fixed bed. The spent coal filter is combusted by feeding it to the gasifier.

The appropriate contacting device for this method is a fixed bed. When fixed bed is used, it is possible to achieve a nearly solute-free gas effluent until the active coal filter in the bed approaches saturation.

The method in [34] is followed. The bed length can be determined by the following relation given in [34], with a bed utilization of 90%:

$$LES = \frac{c_F \phi_v t}{q_F \rho_{bed} \frac{\pi}{4} d_{bed}^2}$$ (8.9)

$$L_{bed} = \frac{LES}{90\%}$$ (8.10)

where:

LES	: Bed length at equilibrium	[m]
c_F	: Concentration solute in the feed	[kg.m^{-3}]
ϕ_v	: Volumetric flowrate of the feed	[m^{3}s^{-1}]
t	: Time to breakthrough	[s]
q_F	: Loading capacity of the adsorbent	[kg$_{adsorbate}$/ kg$_{adsorbent}$]
ρ_{bed}	: Bulk density of the bed	[kg.m^{-3}]
d_{bed}	: Bed diameter	[m]

Since the active coal filter bed acts as safe guard bed when the impurities in the product gas <217> exceed the design criteria of other gas cleaning equipments, two beds are required for the two trains of gas purification. In order to calculate the size of one active coal filter bed, the bed diameter or length must be defined. Here, a bed diameter of 0.5 m is chosen. From the calculation (Appendix 8.2) in MathCAD, a bed length of 14.8 m is required.

8.2.10. CO₂-selective membrane (S202)

The selected membrane is designed and sized using its transport mechanism and its estimated permeability data.

Gas separation by a polymeric membrane (PDMS) is a solution/dilution process, where gases dissolve in the membrane and diffuse through it at different rates, depending on their permeability or solubility in the membrane material.

The flow rate of gas i through a polymeric membrane, J_i, can be written as [43]:

$$J_i = \frac{P_i}{l}\left(p_{f,i} - p_{p,i}\right)$$ (8.11)

where:

P_i	: Membrane permeance of gas I	[mol.m (m^{2}Pa.s)$^{-1}$]
l	: Membrane thickness	[m]
$p_{f,i}$	: Partial pressure of gas i in the feed side	[Pa]
$p_{p,i}$	: Partial pressure of gas i in the permeate side	[Pa]

The driving force of the transport through the membrane is the partial pressure difference between the feed and permeate side. Since Dalton's Law of partial pressures can be applied [34], the partial pressure can be calculated as following:

$$p_{i,j} = y_i P_j = \frac{n_i}{\sum\limits_{i=1}^{n} n_i} P_j \tag{8.12}$$

where:

$p_{i,j}$	: Partial pressure of gas i in the j side	[Pa]
y_i	: Molar fraction of gas I	[-]
P_j	: Absolute pressure in the j side	[Pa]

For the calculation of equipment design a membrane thickness of 50μm is used. There are two types of membrane module, which can be used for this application; hollow fibre and spiral wound module. Since the packing density of hollow fibre module is the highest (10000 m^3/m^2), which means that smaller and cheap equipment can be achieved, the hollow fibre module is chosen and designed [34]. The calculation is performed in MathCAD (Appendix 8.2). This results in a membrane diameter of 6.5 m and a membrane length of 4.3 m.

8.3. Equipment data sheets

The complete equipment summary and specification sheets can be found in Appendix 8.2. Here a simplified equipment summary is tabulated.

Table 8.1: Design summary of the major reactors

EQUIPMENT NR. : NAME :	R201 CFB reactor	R202 Monolith tar cracker	R203 Sour- WGS reactor	R204 Bulk desulphurizer	R205 Zn/Ti Sorbent Regenerator
Pressure [bara] :	7	7/6.4	25/21	21	20.5
Temp. [^{o}C] :	900	900/907	488/543	500	750
Volume [m^3] :	3100	48.1	105.5	141.4	37.7
Diameter [m] :	7.6	2.5	6.2	3	2
L or H [m] :	45.6	3.2	3.5	20	12
Number - Parallel :	10	10	2	2	2
Materials of Construction :	SS, bricks	Incoloy	SS	SS	Incoloy

Table 8.1: Summary continued 1

EQUIPMENT NR. : NAME :	R206 Ultra desulphurizer	C201 NH$_3$/HCl scrubber	C202 Active coal filter bed	S201 Candle filter	S202 CO$_2$-selective membrane
Pressure [bara] :	21/20.5	20.4	17.5/17	6.4	40.5/40.0
Temp. [^{o}C] :	500	25	40	900	95
Volume [m^3] :	73	609.9	2.9	52.8	284.5
Diameter [m] :	3.1	5.7	0.5	3.1	6.5
L or H [m] :	18	23.9	14.8	7	4.3
Number - Parallel :	4	2	2	10	2
Materials of Construction :	Si-SS RA85H	Tray = SS314 Column = CS	CS	Si-SS RA85H	SS

Table 8.1: Summary continued 2

EQUIPMENT NR. : NAME :	E201 Syngas Cooler			
	Coils Water cooled			
Substance - Tubes : – Shell :	 Water Syngas			
Duty [kW] :	1264154			
Heat Exchange area [m^2] :	6872			
Number – Parallel :	 10			
Pressure [bara] - Tubes : - Shell :	 40 6.4			
Temperature In / Out [^{o}C] - Tubes : - Shell :	 80.3 / 685.6 907 / 201			
Special Materials of Construction	Tubes : Al-Bronze Shell : S/incoloy			

Remarks: SS = Stainless steel, CS = Carbon steel, Si – SS = Silicon Stainless Alloy

9. *Waste*

Though the effect of indirect waste (e.g. waste during forestry or transportation) is taken into account in the design selection process, namely in CPD-SAT and SUSDAT, the indirect wastes and plant-household waste will not be discussed in this Chapter. In Table 9.1 direct waste of the supply chain is summarized.

Table 9.1: Waste stream summary

Waste type	Quantity		Application/utilization/action
Baltic States and Sweden			
Wood residues loss	0.5	Mton/a	Protection screen, collection and recycled
Water	5.4	Mton/a	Discharged
Rotterdam			
Ash and char	1.2	Mton/a	Fly ash recycle, road construction application
Spent catalyst	24.2	ton/a	Metal recovery, back to vendor, landfill
Spent Zn/Ti sorbent	943.1	ton/a	Landfill
Water purge	5.7	Mton/a	Recycled to the process after treatment
Salts	0.1	Mton/a	Road salts
Waste gas to atmosphere	0.2	Mton/a	Atmospheric discharge
CO_2	14.0	Mton/a	Atmospheric discharge, storage
Nitrogen to atmosphere	20.8	Mton/a	Atmospheric discharge, storage

9.1. Wastes in Baltic States and Sweden

9.1.1. Wood residues loss

The biomass loss in the chipping and pelletising process is inevitable. The woodchips, sawdust and pellets are biodegradable and a minimum discharged to the environment is not such a big problem. It is of great importance that the amount lost is minimal. To minimize the loss protection screen can be installed around the equipments. The biomass in the scattered in the factory area can periodically be collected and reintroduced in to the machine.

9.1.2. Water

The pelletising process also produces water originated from the wet woodchips and sawdust. The water coming out of the pelletiser also contains a small amount of wood particles. This water stream can be discharged into the environment since it is of natural origin. Extra precaution can be taken by applying filtration and also by taking and testing water sample periodically.

9.2. Wastes in Rotterdam

9.2.1. Char

A small percentage of the biomass, approximately 6 %, is loss during the syngas production. There are two major biomass depletion points, along the 'storage to gasifier' line and at the internal CFB cyclone. Biomass loss around the storage can periodically be gathered and reintroduced in the process system. At the internal cyclone unreacted biomass, in the form of carbon, comes out with the fly ash. The unreacted biomass in the fly ash will be considered as part of the fly ash and will be discussed in the ashes section.

9.2.2. Ash

Ash composition coming out of a CFB is strongly dependent on the type of fuel, the gasification condition and reactor. Utilization of CFB ash is therefore not a very certain matter. The ash can become a valuable raw material for other processes or a very costly hazardous waste.

Construction applications have been identified as one of the major uses for CFB ashes. However, ashes resulting from a gasification of untreated wood have a low SiO_2 and Al_2O_3 fraction and a high CaO fraction, which will limit their application/utilization. A typical ash composition of untreated wood [57] can be seen in Table 9.2.

Table 9.2: Ash composition of untreated wood from Phyllis database

Ash components	wt%	Ash components	wt%
CO_2	-	Al_2O_3	0.7
SO_3	-	CaO	28.6
Cl	-	MgO	6.7
P_2O_5	11.6	Na_2O	0.9
SiO_2	2.8	K_2O	23.9
Fe_2O_3	0.4	TiO_2	0.1

In the Netherlands, three main applications of gasification ashes can be identified [39], namely as filler in cement and concrete, as raw material for the production of port land/cement clinker and as filler in asphalt.

In a CFB two sorts of ash can be distinguished, bottom ash and fly ash. Bottom ash, which is a result of sintering of the ash particles, is collected from the bottom of the gasifier. Due to the use of sand as heat carrier, the bottom ash also contains a small fraction of sand particles. The fly ash is carried along with the gas phase and is removed by the candle filter. The fly ash usually contains unburned carbon that still has a high value.

The CFB ashes in general cannot be used as raw material for cement industry due to the typically low SiO_2 and Al_2O_3 [58]. Application of the bottom ash in the road construction sector is the most relevant large-scale application. A certification of the bottom ash has to be acquired for this application, where the main concern is its leaching behaviour. Bottom ash can also be used as a light-weight synthetic aggregate in concrete blocks. Application as soil stabilizer is also possible.

The CFB fly ash still contains the valuable carbon so that the application as asphalt filler seems to be a misapplication. Reintroduction of the fly ash into the gasifier is a good

option. Another option is to upgrade the carbon content into active carbon that can be used in the process [59]. A fly ash after burner is also possible.

CFB ash streams can also be used to stabilize waste streams from a variety of processing operations [60]. This stabilization includes solidification and fixation of sludge materials for land filling, neutralization of acidic wastes, and municipal sludge waste sludge. For each of these applications, the suitability of CFB ash is enhanced by its free lime content. The infrastructure of the plant area should be good for transporting the bottom ash from the plant, considering the amount of ash that can pile up and increasing health hazard in the plant area.

Health considerations must also be taken into account in handling and transporting ash (internal and external), especially of fly ash. Utilization of vacuum cleaners and particulate detectors can be executed.

9.2.3. Sorbent and spent catalyst waste [31][61]

The sorbent and spent catalyst wastes are typically disposed off using a service from a third party. This service requires extra expenditure that is an extra burden for the process. The catalyst used in this process is assumed to have a lifetime of 5 years. Disposal is done periodically, every 5 years. The sorbent waste on the other hand is a continuous waste that will temporarily be stored, up to some extent, before transport. Continuous sorbent waste disposal requires a good and consistent infrastructure, considering the amount of sorbent waste generated.

A type of catalyst with over 10% of a single heavy metal (ZnO, or Ni on alumina) is relatively easy to dispose of, since both the disposal company and the process are having a positive net return.

In some cases, spent alumina catalyst can be resold to original vendor, but it is usually applied for landfill. The spent sorbent and the CoMoS is typically disposed off as landfill, e.g. for the coal mining industry. Depending on composition, controlled landfilling might be done. Landfilling typically has lower cost but incurs a risk of future liabilities for the process. In case the spent catalyst needs to be sent out of the country, often long-lasting government procedures and interpretation of the Basel Convention can delay the disposal process significantly.

9.2.4. Wastewater and salts

The wastewater stream generated in the plant is processed in the wastewater treatment. After the treatment the water is recycled in to the process. Due to the relatively clean untreated wood as gasification fuel, it is expected that the salts produced do not contain heavy metal. The barrier reactors of the ultra desulphurizer also make sure that particulate free wastewater from the scrubber can be realized. The volatiles (NH_3, CO_2, H_2S and HCN) could be stripped using steam and fed back into the gasifier. The resulting salts can be utilized as road salts or as salt bath in the metal industry depending on the curing agent.

9.2.5. Air pollution

The main source of air pollution in the process is the off gas from the Claus unit. The after flaring, the waste air consists of mainly N_2 and CO_2 and a minute amount of SO_2.

The expected SO_2 level in the waste stream is below the atmospheric discharge level according to the EU directive of 800 mg/n m^3 (= 262 ppmV) [62].

Another substance that is discharged to the atmosphere is CO_2. Since the feed of the process is biomass the CO_2 discharge will not contribute to an increase of the CO_2 level in the atmosphere. It should be noted that CO_2 storage is highly recommended. This will increase the sustainability character of the process.

Nitrogen, which is produced in the air separation unit and not applicable in any other part in the process, is also considered as waste. Though it is 'freely' discharged in to the air, nitrogen can be very dangerous for the surrounding people. Nitrogen is odourless and can push oxygen away without notice resulting in suffocation. The discharge point should then be at a high point in the plant and leakage should be prevented.

TUDelft

10. Process Safety

The evaluation of the process safety of the design is performed by using Dow's Fire & Explosion Index [63] and Hazard and Operability (HAZOP) study [53]. The F&EI is used for evaluation for realistic fire, explosion and reactivity potential of process equipment and its contents. Therefore, the safety hotspots of the design can be seen. After F&EI, an analysis of HAZOP study is performed to identify the hazard and operational risk and the actions reducing the risk. Both tools are applied for all major equipments, except the wastewater treatment, the electricity plant, the air separation plant and the Claus plant.

10.1. Risk analysis calculation by F&EI

As described in [63], the procedure of risk analysis calculation is performed. The risk analysis calculation by F&EI consists of a Fire & Explosion Index form, a Loss Control Credit Factors (LCCF) form and a process unit analysis summary. These forms can be found in Appendix 10.1. The results of these forms are summarized in a manufacturing unit risk analysis summary, as given in Table 10.1.

Table 10.1 Manufacturing unit risk analysis summary

Name of Unit	Basic component	MF	PF	F&EI Index	Value of Area Exposure [M€]	Base MPPD [M€]	LCCF	Actual MPPD [M€]	MPDO [days]	BI [M€]
Chipper (A101)	Wood dust	16	0.21	3	0.45	0.08	0.88	0.07	5	0.27
Pelletiser (X101)	Wood dust	16	0.16	3	0.81	0.15	0.88	0.13	8	0.40
Wood warehouse	Wood dust	16	0.37	6	0.03	0.01	0.88	0.01	1	0.07
Storage column	Wood dust	16	0.55	9	5.57	2.00	0.81	1.62	34	1.75
Lock hopper (V201)	Wood dust	21	0.19	4	8.98	3.14	0.76	2.39	43	2.20
Circulating Fluidized Bed reactor (R201)	CO	21	3.06	64	68.85	43.38	0.73	31.66	198	10.16
Candle filter (S201)	CO	21	1.34	28	3.05	1.37	0.80	1.10	27	1.39
Monolith tars cracker (R202)	CO	21	2.10	44	32.05	16.02	0.75	12.06	112	0
Syngas cooler column + turbine	CO	21	1.33	28	32.85	14.78	0.69	10.22	101	5.20
Sour water-gas shift (R203)	CO	21	2.18	46	99.37	49.69	0.75	37.39	218	11.22
Bulk desulphurizer (R204)	CO	21	1.92	40	19.48	9.74	0.73	7.11	82	4.19
Zn/Ti sorbent regenerator (R205)	CO	21	4.40	106	8.98	6.01	0.72	4.35	61	3.13
Ultra desulphurizer (R206)	CO	21	1.71	36	20.29	12.78	0.73	9.33	96	4.93
NH3/HCl scrubber (C201)	CO	21	1.90	40	4.04	2.02	0.74	1.50	33	1.67
Active coal filter bed (C202)	CO	21	1.33	28	1.89	0.85	0.75	0.64	20	1.01
Compressor, 6.3 bar to 40 bar	CO	21	1.97	41	1.08	0.54	0.78	0.42	15	0.79
CO2-selective membrane (S202)	CO	21	1.33	28	127.65	57.44	0.77	44.10	241	12.37

The F&EI procedure to appoint several penalty factors is described in the Dow's Fire & Explosion Index Classification Guide [63]. The F&EI can be divided in two parts: the general process hazards (GPH) and the special process hazards. These two consist of

several factors relating to the hazards analysis. When these factors are irrelevant for the design, the value will be zero. Some factors are assumed to be zero, because these factors can only be employed after the plant is operating, such as leakage-joints and packing of plant units.

The first step of the analysis is to identify the most dangerous component in the process unit that is present in a considerable amount (>5 wt%) and to give it a Material Factor (MF) based on its flammability and reactivity. In most process units, CO presents in large amount and it gets a MF of 21. For the pre-treatment step, there is no flammable gas or liquids, but the wood residues have an explosion danger due to the sawdust. Therefore it gets a MF of 16. The temperature dependency is taken into account, but it does not change the MF.

Furthermore, the Loss Control Credit Factors are taken into account as protective measure to prevent serious incidents and to reduce the probability and magnitude of a particular incident. The three categories of loss control features are Process Control (C1), Material Isolation (C2) and Fire Protection (C3). When the credit factor is irrelevant to the design, a credit factor of 1.00 is used. Determination of these loss control features is based on the common engineering sense, since the design is not developed completely in this stage of the design. This analysis will not give high accuracy, but at least it can give a picture about what kind of measures can be applied to reduce or control the unit hazards.

After all, the process unit risk of each unit operation is analysed. This gives additional risk information, which is determined in the F&EI, the LCCF, the Area of Exposure, the Damage Factor and the Value of Production for the Month. For the calculation of the value of Area of Exposure, the major equipment cost estimated in Chapter 11 is used without correcting the installed cost using Engineering Estimating Installation Factors. Since no escalation values after 1995 are given in the Dow's Fire & Explosion Index Classification Guide, a yearly increase of 10 is assumed. The plant is assumed to be built in 2010, where an escalation value of 528 is estimated, and to start running the plant in 2015, where an escalation value of 578 is estimated. This is maybe a rough estimation, but it will give indications about the process unit risk.

Finally, it can be concluded from this analysis that the process units have a range of degree of hazard between light and intermediate [63]. Moreover, it can be seen clearly that a process unit with high temperature operation like Zn/Ti sorbent regenerator, where dust or solid particles, is the most dangerous since dust explosion can occur. A complete control structure must be installed for these units to prevent the dust explosion, like a fast flow controller for the air stream to the Zn/Ti sorbent regenerator. Process units like the CFB, the monolith tar cracker, the sour water gas-shift reactor and the CO_2-selective membrane, which have large equipment cost, have the most business interruption if they have problems or are broken and needed for repairing or replacement. This can be seen in Table 10.1, in the values of Maximum Probable Day Outage (MPDO) and Business interruption (BI). Therefore periodic maintenance is required. Since carbon monoxide presents in large amount in the whole plant, a safety measure like leak detector must be installed for the worker's safety. Furthermore safety measures, such gas alarms, gas discharge to a flare and gas strippers should be installed.

10.2. Analysis of HAZOP study

With use of the guidewords like NO/NOT, MORE, LESS, OTHER THAN and REVERSE the different scenarios for all major equipments are considered. Using the estimated consequences of the different scenarios the safety measures or other actions are determined to prevent hazards and control the process safety. A complete analysis of HAZOP study is given in Appendix 10.2.

As evaluated in the risk calculation by F&EI, the Zn/Ti sorbent regenerator has the highest degree of hazard. Therefore, only this regenerator will be explained and discussed in this section.

Two main hazards in the Zn/Ti sorbent regenerator are the possibilities of runaway reactions and dust explosion. These hazards are instigated by uncontrolled temperature and pressure ([64][65]). The consequence is that those reactors can explode and the whole plant must be shutdown. Several measures can be taken in order to prevent these hazards. A good control structure for temperature is required and must be installed for this regenerator, where the temperature can be controlled by adjusting or closing the valve of the air streams to Zn/Ti sorbent regenerator in order to prevent the deterioration of the hazards. Moreover a busting disk must be installed to reduce the pressure when the pressure increases rapidly.

More details on the operability of major equipments can also be found in Appendix 10.2. Due to the purposed measures, the hazards and risks can be reduced at acceptable level within the battery limits of the design.

TU Delft

11. Economy

Based on the mass and energy balances from the ASPEN PLUS model, an economic evaluation of the design was made of the capital and operational cost. As a guideline, Lang's method in Chapter 6 of Coulson & Richardson's "Chemical Engineering" [53] is applied for the economic analysis and evaluation.

11.1. Investment (Once-off)

The capital costs have been estimated using the following equation:

$$C_2 = C_1 \left(\frac{S_2}{S_1} \right)^R \qquad (11.1)$$

where C_2 = capital cost of equipment with capacity S_2
C_1 = capital cost of equipment with capacity S_1
R = scale factor, between 0 and 1, indicating the level of "economy of scale".

Table 11.1 shows the purchase cost of the major equipment in the supply chain. Transport like trucks and bulk sea vessels are not fixed capital, i.e. Shell will not purchase all the necessary ships and trucks. Instead, transport will be on a contract basis, and it can be found under *variable operational costs*. Most of these costs have been calculated based on prices from recent studies and articles.

Table 11.1: purchase cost of the major equipment items

Units	Number of units	Purchase cost [M€$_{2004}$]
Chipper	21	10.5
Pelletiser	497	447.3
Circulating Fluidised Bed	10	767.0
Candle filter	10	34.0
Monolith Tar Cracker	10	357.0
Sour Water-Gas Shift Reactor	2	221.4
Bulk desulphurizer + regenerator	2	63.4
Ultra desulphurizer	4	90.4
Ammonia/HCl Scrubber	2	9.0
CO2-selective Membrane	2	142.2
Compressor	6	28.8
Air separation plant	1	139.2
Claus plant	1	9.2
Waste water treatment	1	0.4
Steam turbine	2	60.4
Storage tank	70	6.2
Syngas cooler	10	64.0
Active coal filter bed	2	4.2
Total		**2,454.6**

A detailed overview of the major equipment purchase cost can be found in Appendix 11.1. The total physical plant cost (PPC) is then calculated from the total purchase cost of equipment (PCE) and Lang factors 1 to 9 (Appendix 11.2). The total fixed capital is the

PPC + the indirect costs, which are calculated from the PPC. The working capital is estimated according to rules of thumb, and the fixed capital and the working capital together make the total investment required. All this is summed up in the Table 11.2.

Table 11.2: Overview of investment costs

Investment		Cost [M€$_{2004}$]
Major equipment, total purchase cost (PCE)		2454.6
Total physical plant cost (PPC)	= PCE x 3.40	8345.6
Indirect costs (IDC)	= PPC x 0.45	3755.5
Total fixed capital (FCC)	= PPC + IDC	12101.2
Working capital (WC)	= FCC x 0.066	674.6
Total investment	= FCC + WC	**12775.8**

11.2. Operating Costs

Operating costs are divided in fixed and variable operating costs. Fixed costs include items like maintenance, operating labour, supervision etc. A complete list can be found in Appendix 11.3. In Appendix 11.4, the variable costs are described. Variable costs are the costs for feedstocks, utilities and wastes. These two costs are the direct costs of producing the product at the plant site. In addition to these costs, the site will have to carry its share of the company's general operating expenses. Table 11.3 shows the operating costs.

Table 11.3: Overview of operating costs

Operating cost	Cost [M€$_{2004}$/a]	Cost [€$_{2004}$/GJ$_{syngas}$]
Fixed operating costs	2854.4	12.4
Variable operating costs	665.4	2.9
Indirect operating costs	528.0	2.3
Total operating costs	**4047.9**	**17.6**

11.3. Income

The plant makes two products, and the income from their sales is shown in Table 11.4.

Table 11.4: Overview of income from products

Product	Amount [Mton/a]	Income [M€$_{2004}$/a]
Syngas	11088000	1430.4
Sulphur	7488	0.3
Total income		**1430.6**

11.4. Cash Flow

The annual Cash Flow is the difference between annual Income and Operating Costs. Table 11.5 shows the cash flow.

Table 11.5: Cash flow

	[M€ @ 2004]
Annual income	1430.6
Annual operating costs	4047.9
Annual net cash flow	**-2617.3**

As can be seen from Table 11.5, there is a large negative cash flow, caused by too high operating costs and/or too low income.

11.5. Economic Criteria

Table 11.6 shows the assumed plant lifetime and start-up time, as well as the Rate On Return. The ROR is of course negative, caused by a negative cash flow.

Table 11.6: Life-time and Rate On Return

Variable	Value	Source
Time for design, build and start-up of plant	5 years	based on Shell estimates for Qatar plant [16]
Plant life-time	20 years	[20]
Rate On Return	-16%	

11.6. Cost Review

From the economic criteria above it is clear that this design will not be economically viable, at least not with the assumptions used to calculate these criteria. Hot spots in the economic evaluation of this project are the major equipment costs, the capital charges and the syngas price.

The "Lang Method" [53], used here to evaluate the economics of the process, depends strongly on the major equipment costs. The major equipment costs determine the fixed capital costs, and these again strongly determine the operating costs. Thus, the major equipment costs are an important parameter.

The equipment costs calculated here are indications; specific equipment prices or benchmark data are hard to find, and so their accuracy is questionable. The following figure shows the division of the major equipment costs between the different unit operations.
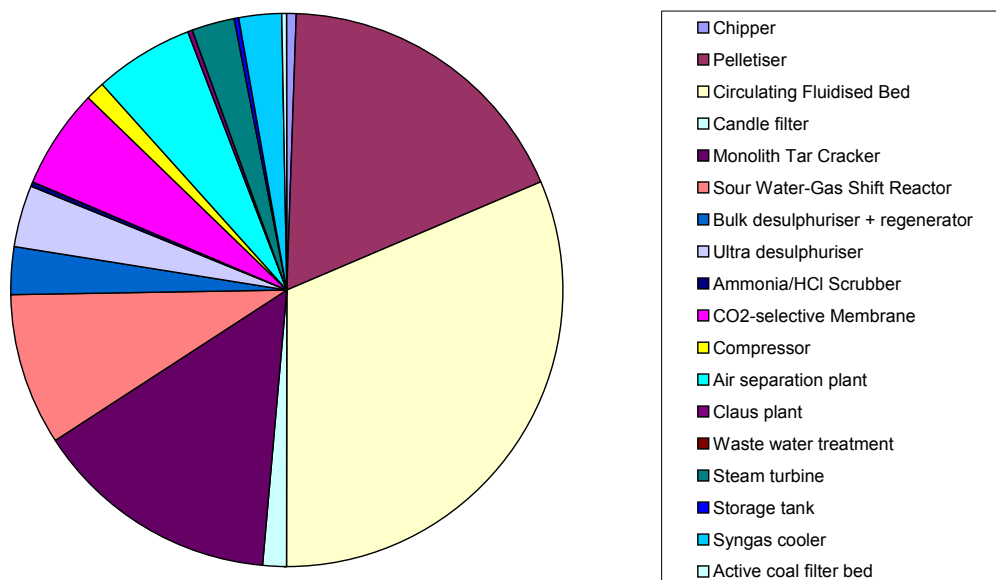

Figure 11.1: Major equipment costs

As can be seen from Figure 11.1, there are some very expensive units and some very cheap units. Table 11.7 shows the most and the least expensive equipment.

Table 11.7: Most and least expensive equipment

Most Expensive Equipment	Percentage of total equipment costs	Least Expensive Equipment	Percentage of total equipment costs
Circulating fluidized beds	31%	NH$_3$/HCl scrubbers	0%
Pelletisers	18%	Chippers	0%
Monolith tar crackers	15%	Active coal filter beds	0%
Sour water-gas shift reactors	9%	Claus plant	0%
		Waste water treatment	0%
		Storage tanks	0%

It is difficult to say whether these costs are in proportion to each other. The CFB's seem very expensive, as well as the monolith tar crackers. The costs for pelletisers can be explained by the fact that there is no economy of scale for these units. Due to their small scale, almost 500 pelletisers are required. Maybe in the nearby future, it can be expected that there is a significant increase in pelletiser size, which could greatly reduce costs.

On the other hand, the least expensive units seem out of proportion as well, accounting only for less than 0.5% of the total equipment per unit. Most of the equipment costs come from recent published articles.

The operating costs are 365 €/ton syngas, while the syngas is sold for only 129€/ton. This means that the price for syngas is simply too low.

These high operating costs are not so much caused by the variable cost, i.e. the feedstock costs, waste costs etc. The major contributor to the high operating is the capital charges, which contributes to 45% of the total operating costs.

11.7. Sensitivities

Since there is a negative cash flow, it has no use to look at any economic criteria now. Figure 11.2 shows the sensitivity of the (negative) cash flow with respect to major equipment costs, circulating fluidized bed price, wood price, syngas price, waste price and capital charges. A change of −10% is used. (A change of +10% gives the same results, only then inverted).

As can be seen from Figure 11.2, the major equipment costs have a large influence on the cash flow, and thus on the overall economics of the process. A 10% change in the CFB price alone has a change of 8% on the cash flow. On the other hand, the wood price only has a small influence on the cash flow; the waste price has almost no influence, since the amount of waste is very small. The variable costs are mainly determined by the biomass and electricity costs.
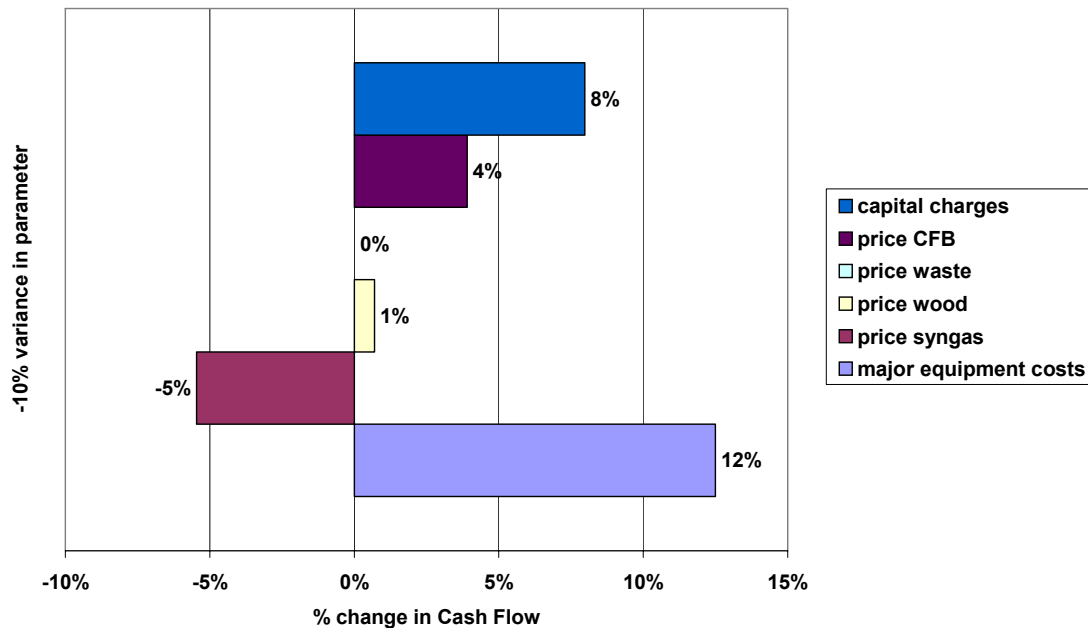
Figure 11.2: Sensitivity analysis

11.8. Proposed cost reductions

The changes in economics required for an economically viable process will be a combination of multiple changes. An increase in syngas price and therefore an increase in FT fuel price could be possible in the future if governments decide to cut the taxes on FT fuels. The current fuel price consists for almost 70% of taxes [3]. If there would be no taxes on the FT diesel, its price could rise with 100/30 = 333% to arrive at the current diesel price.

As is mentioned in Chapter 5.6, a better utilization of steam from the FT plant, through extensive heat integration, could further decrease the Rotterdam plant power consumption.

There are no costs calculated for CO_2 in this economic evaluation. The proposed CO_2 taxes do not apply for processes using biomass as feedstock [67], which is the case for this process. If it is possible in the future to sequestrate CO_2, this process could even earn from the CO_2 it produces by selling the emission allocation. And this is not unlikely, since this process produces an almost pure stream of CO_2, which is now discharged into the air. In the case that CO_2 is sequestrated (e.g. in the geological reservoirs), a breakeven CO_2 credit of €10 per ton CO_2 can be achieved [69], when CO_2 tax of €15 per ton CO_2 can be assumed [67]. This will have an increase in syngas price of about 5% on the plant economics.

Capital charges are set at 10% of the Fixed Capital Costs, according to the suggestion of Coulson & Richardson's [53]. However, the same source also suggests an alternative way of calculating the capital charges, and that is to set it at 2% above the current minimum lending rate. The lending rate has been around 4.5% the last few years in the European Union [68]. A lower capital charge is also justifiable since a plant life of 20 years is taken, giving a lower depreciation rate than the previously used 10%.

TUDelft

And thus, the most realistic way to make this process economically viable is a combination of changes:
1. A decrease in major equipment costs.
2. An increase in syngas price
3. Income from selling CO_2 allocation
4. A decrease in capital charges
5. An increase in plant energy efficiency

The major equipment costs are changed as follows: the price of the five most expensive units is lowered with 20% and the price of the five least expensive units is increased with 50%. This is done to get a more even distribution of costs between the different equipment. This leads to an overall decrease in major equipment costs of 18%.

The syngas price is increased with 200%. This means the FT diesel could compete with fossil diesel if a reduction of taxes on FT diesel from 70% tot 40% is imposed. This could become reality when governments want to stimulate the use of "green" diesel, like FT diesel. It would be a form of subsidizing the use of biomass.

The income from CO_2 storage is taken as 10€/ton [67]. The costs for storage have not been taken into account. The capital charges are lowered to 6.6%, 2.1% above the average marginal lending rate from the past four years [68]. The power consumption is lowered with 20%. These changes result in a break-even of 24 year after the start of the project.
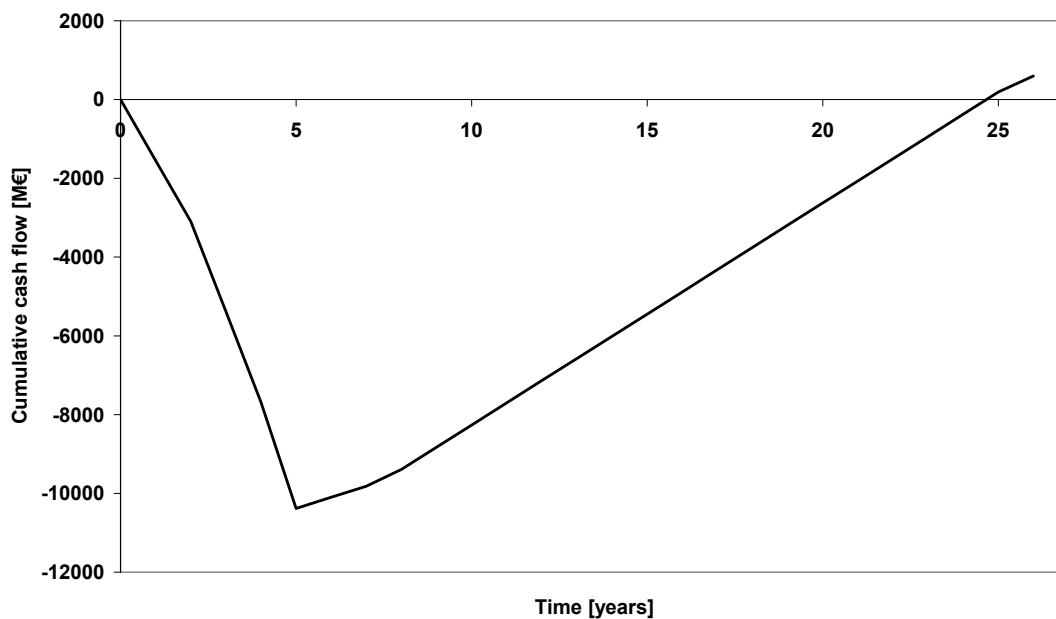

Figure 11.3: Project cash-flow diagram

The data from this diagram can be found in Appendix 11.5. This diagram is based on a design and building time of five years, and a plant life of twenty years. Furthermore, it is assumed that the first train of the process as described in Section 3.2.2 in Rotterdam will be finished after these first five years, and that the second train becomes operational after

two more years. So, production is 4000 MW in the first two years of operation, then one year of 6000 MW, and then 8000 MW all the way to the end.

It should be noted however that 8000 production hours per year, as arranged with the principals and used in the calculations, is very optimistic values for this kind of plant. Personal communication with the NUON power plant in Buggenum showed production hours ranging from 5000-6500 hours, after five years of operation.

12. Creativity and Group Process Tools

In this chapter the use and outcome of the creativity and group process tools are reviewed. The Delft Design Matrix is used as guideline for our work process, especially in the first 4 phases of our design. In this chapter the efficiency of the creativity and group process tools is reviewed. The creativity and group process tools used in the CPD are taken from our *BAWEL* tool, which is explained in Appendix 12.1.

As said in previous chapters, during this design project, two sustainability tools are tested and applied to the design process. These tools have had significant influences on the design decisions that are made. The first tool is CPD-SAT. This tool helps to make a selection for a supply chain option out of 5 different biomass source alternatives. Those 5 alternatives were again selected from a group of 20 possible supply chain alternatives. These initial alternatives are generated from creative ideas through brainstorming and survey of the stakeholders' opinion. The results of these brainstorm sessions and the result of CPD-SAT can be found in Appendix 2.2 and section 2.2, respectively.

The second sustainability tool, SUSDAT, helps to make a selection for a chain of unit operations out of 7 different alternatives. These 7 different chains of unit operations are composed of all possible unit operations generated from creativity after several brainstorming sessions and some literature research. What applied for the first tool, applies here as well; a lot of time has been put in the testing of many possible alternatives, of which all of them are composed by own engineering common sense. The results of these brainstorm sessions and the result of SUSDAT can be found in Appendix 2.9 and section 2.3, respectively.

As mentioned above and in Chapter 1, both sustainability tools require a lot of time since they were still in developing phase when they were applied in this design project. Therefore, time is spent on helping the developers of the tools with comments and some ideas how to improve these tools for easy and friendly use.

Another form of creativity is the surveys that are held to get the opinion of the stakeholders. The results of these surveys are used in order to generate new ideas or alternatives that are not considered. These opinions are considered as useful input to determine. The questionnaires can be found in Appendix 2.6 and Appendix 2.8.

Furthermore, a discussion with people, who have environmental study background, is held. Some useful tips are generated during the brainstorm session with them, like the produced noise due to the increasing number of ships, the flexibility of biomass sources to avoid the dependency of one biomass source or the fact that the C-cycle will be not closed completely easily since large amount of biomass is involved, for more details about the discussion see Appendix 12.5.

An excursion is organized to visit a coal power plant in Buggenum (Roermond), in order to get some feedback and observe the similar process in practice. Also, a lecture about

CO_2 emission trading from KPMG is attended. Both the excursion and the lecture give some valuable information about process details, economics and regulations.

As said above, the Delft Design Matrix is used as guideline for the work process, especially in the first 4 phases of our design. Phases 5, 6 and 7 were performed without following the DDM precisely. This is caused by two factors: the application of both tools requires more time than planned, and are also overlapping different phases of the Delft Design Matrix, which lead to indistinctness about which phase the group is in. Another point is that the DDM is not always very clear.

The Advanced Activity Assistant (AAA) is used to plan and report the activities. A summary of important activity in AAA can be found in Appendix 12.2.

Direct results of most of the creativity tools and group process tools are sometimes hard to determine. Appendix 12.1 gives an overview of the methods used during this CPD project. The methods with clear and direct results will be described in Appendix 12.3.

The best example of direct results from the creativity tool is the brainstorm session. Brainstorm sessions were held on 26th, 28th of April and 4th of May, sometimes with the presence of the creativity coach. During the first brainstorm session, alternatives are generated, for example for the different cases investigated in the two sustainability tools, as stated above.

The Belbin tool is used three times; at the start, in the halfway and at the end of the project. The Belbin tool analyses the different roles of people in a group. The results of Belbin test concerning the group's maturity process are summarized in Figure A.12.4.1. A complete the results of three Belbin test can be found in Appendix 12.4.

At the start of the design process every role, except "Plant", is fulfilled in the group. Generating new ideas and strategies, especially on important subjects and searching for openings in problems that the team is still confronted with are strong points of a 'Plant'. For the CPD project this person is very important. The use of different group work processes tools and creativity tools will help us to fill this gap. One of the goals of the creativity tool is to help us to generate new and creative ideas.

Halfway the design process the role of 'Plant' emerged; all group's role are represented. This phenomenon reflected the group's maturity process where the group tried to compensate for the quality it was lacking. As result the profile became broader.

At the end of the design process, some changes in the group roles can be observed, as shown in Figure 12.1. These changes maybe can be explained by the fact that the design process is more focused into the details of the design. Lots of calculation and simulation are performed. It means also that less brainstorming sessions are held in the last three phases. Some important brainstorming session these last phases are solving design bottlenecking when the chosen unit operations cannot be used for the final design and identifying hazards and operability issues for HAZOP study. Since a lot of design details must be done, the role of Company Worker becomes the strongest point in these last phases.
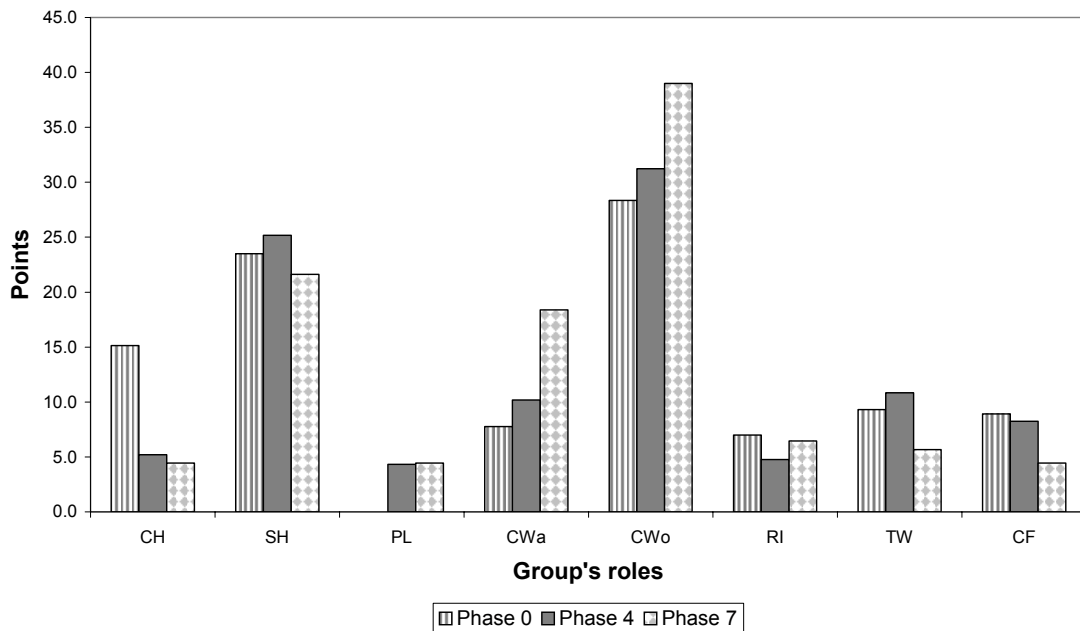
Figure 12.1: The results of Belbin test concerning the group's maturity process

Finally, it can be seen that the group grows continuously during the design process. It is also shown that all group members are flexible to fulfill the group roles when they are needed. It is also experienced that the group process becomes mature in time. Problems are solved more structurally and easily. Due to several socializing occasions, the group members can understand each other better and the design process goes very well.

13. *Conclusions and recommendations*

In this chapter the conclusions made during and at the end of the CPD3309 assignment are summarized. The first part will give conclusions concerning the design and will comprise good and bad aspects of the design. The second part will present recommendations to improve this design with several alternative possibilities. The third part will present conclusions about the CPD-SAT and the SUSDAT tools.

13.1. *Conclusions about the design*

The supply chain from wood to syngas is designed as an alternative to normal production of syngas from methane. This has resulted in a relatively sustainable design, producing little waste, and with a thermal efficiency of 87 %. In the project description specifications for the produced syngas are set and Table 13.1 shows that these specifications are met by the designed process. However it should be stated that the results have an uncertainty of about less than 40%. For conceptual design 40% uncertainty is achieved. Due to the use of the sustainability tools, the uncertainty declined a bit.

Table 13.8: Specifications, desired and achieved

Impurity	Removal Level	Achieved level
H_2S + COS+ CS_2	< 1 ppmV	998 ppbV
NH_3 + HCN	< 1 ppmV	625 ppbV
HCL + HBr + HF	< 10 ppbV	9 ppbV
Alkaline Metals	< 1ppbV	Essentially zero
Solids (soot, dust, ash)	Essentially completely	Essentially zero
Organic compounds (tars including BTX)	Below dew point	Below dew point
Class 2 tars: phenol, pyridine, thiophene	< 1ppmV	~ 0
Objectives	**Desired level**	**Achieved level**
Production rate	334 kg/s	340.9 kg/s
H_2/CO ratio	2	2.0
Inerts	below 5%	3.5%

The strengths of the design are:
- Use of sustainability tools ensured a sustainable design.
- The plants capacity is 1.5 % of the European market.
- Due to the use of regenerable Zn/Ti sorbent for desulphurization, less waste is produced.
- The HAZOP study shows a low to medium risk over the design, so it is a relatively safe process.
- The produced diesel has high quality and will meet the future standards.
- The process is robust due to two separate production trains and therefore less sensitive to equipment failure.

The weaknesses of the design are:
- The wood residues come from different countries, relatively far away from The Netherlands. This increases the risk of an unstable feedstock supply.

TUDelft

- The Circulating Fluidized Bed (CFB) reactor is designed solely for wood. A CFB is quite inflexible compared to an entrained flow reactor, where different biomass can be used as feedstock.
- The HAZOP study shows that the Zn/Ti sorbent regenerator has the highest degree of hazards (intermediate level), because there is a certain chance of dust explosions.
- The economic analysis shows a barely economically feasible process, which gives high financial risks.
- Operation hours of 8000 hours will be difficult to achieve for this biomass gasification plant, especially in the first years of operation.
- A very large volume of nitrogen is produced, which has no market and is therefore not valuable for the process.

13.2. Recommendations for future work

Several ideas have been generated on how to further improve the design and issues that are not taken into account in the conceptual design:

- The entrained flow reactor is more robust in dependency on feedstock composition. So the possibility of an entrained flow reactor and the influence of a varying feedstock can be further investigated.
- The steam provided by the FT process to the gasification process is not fully utilized. By utilizing this stream in the heat integration, a lower power consumption can be achieved.
- The FT process, as it is, requires a very stable syngas feed. If the FT process is performed as a once through process the unconverted heavy wax can be used for heat/electricity generation. This mode makes it possible to have less strict specification requirements (e.g. inerts like CO_2 and N_2) of the syngas produced in the gasification process.
- The synergy with surrounding plants on the "Tweede Maasvlakte" has to be investigated.
- The SHE analysis is not done completely; it is limited to the Safety aspect. The complete SHE analysis should be done in future works.
- The equipment design performed in this project is designed quite summarily, thus more details on the design can be added to the equipment. The kinetics of the CFB is still unknown and difficult to model. A model for the CFB is still to be developed.
- The possibility of building the plant in the land of the feedstock origin reduces costs and improves the economic feasibility.
- The carbon dioxide produced in the process is very pure and can be sequestrated in geological reservoirs or other alternatives for sequestration can still be developed. Using the emission trading of the Kyoto Protocol, the CO_2 allocation can be sold to the refineries or other companies that have large CO_2 emission.

In the conceptual design of the supply chain of syngas from biomass, the main uncertainties are:

- The supply of biomass is not secured for a period of 20 years. If the Baltic States or Sweden decides to utilize their own natural resource, a big problem arises for the plant in Rotterdam.
- The composition of the stream leaving the CFB is estimated from literature. This stream is highly dependable on feed composition, reacting temperature and reacting pressure and therefore the process needs a correct model to predict this.
- A lot of uncertainty exists on the kinetics used in modelling the tar cracker.

13.3. Conclusion and recommendation about the tools

The CPD-SAT tool can be used in future CPD projects in phase 1 to 3. It is a helpful tool in adding a certain degree of sustainability to a design.

The SUSDAT tool in its present format is inappropriate to be applied in phase 4 of a CPD project. It consumes too much time, because a lot of details of many alternatives of unit operations are required.

Nevertheless the CPD3309 project benefits from using both tools, despite the fact that most of the project time is spent for the application of both tools. The last part of the project is performed with less accuracy than a normal CPD project, since this CPD project focus lies on sustainability of the design, not on the equipment design.

Both tools can be improved by using databases. For the CPD-SAT this means databases for the SLCA and SHE analysis. The SUSDAT tool can be improved by providing process specific databases of general unit operations to reduce time needed for calculating the mass balances and determining the values of its indicators.

List of Symbols

Symbol	Description	SI Units	Symbol	Description	Unit
A	Absorption factor	-	p	*Partial pressure*	*atm*
A	Surface area	m^2	P	Permeance	mol.m/(m²Pa.s)
A	pre-exponential factor	m^3/kgcat-h; 1/s; m^3/mol-s	P	*Pressure*	*bar, Pa, atm*
			q	Loading capacity	kg/kg
c	*Concentration*	M	r	Rate	mol/m³-s
C	Concentration	mol/m³	R	*Gas constant*	*J/mol-K*
d	*Particle/bed diameter*	*m*	t	Break through time	s
D	*Equipment diameter*	*m*	T	*Temperature*	*°C, K*
E_a	*Activation energy*	*KJ/mol*	V	*Volume*	*m³*
G	Gas flow rate	m³/s	W	*Weight*	*kg*
H	Enthalpy	J/mol	x	Liquid molar fraction	-
H	*Height*	*m*	y	Vapor molar fraction	-
H	Henry's constant	atm			
$\Delta_{sol}H$	Enthalpy of solution	kJ/mol			
k	Rate constant	1/s	Greek	Description	SI unit
k_H	*Henry's Law constant*	*M/atm*			
K	Equilibrium constant	-	Δ	Difference	-
K	Equilibrium ratio	-	ε	Voidage/porosity	-
L	Membrane thickness	m	μ	Viscosity	Pa-s
L	Length	m	ρ	Density	kg/m³
L	Liquid flow rate	m³/s	τ	Residence time	s
LES	Bed length	m	u	(Superficial) velocity	m/s
N	*Number of …*	-	ϕ_V	Volumetric flow rate	m³/s
N	Number of stage	-			

TUDelft

Subscript	Description	Subscript	Description
298	At 298 K	G	Gas
1173	At 1173 K	i	Component i
bed	Bed	j	j side
cat	Catalyst	p	Permeate side
CFB	CFB reactor	R	Reactor
downer	Downer	Riser	Riser
eq	Equilibrium	tube	1 tube
f	Feed side	tubes	Bundle of tubes
f	Fluid, gas		
F	Feed	Superscript	Description
face	Face (candle filter)	0	Standard condition (1 bar 298K)
filter	Candle filter		

TUDelft

References

[1] http://www.ecn.nl/biomassa/research/poly/index.en.html, ECN Biomass, *Directive on the promotion of the use of bio-fuels or other renewable fuels for transport*, European Parliament, May 2003, visited: 27 July 2004

[2] http://www.novem.nl/default.asp?menuId=10&documentId=115827, C.N. Hamelinck, *Outlook for advanced biofuels,* (PhD thesis), 2004, visited: 27 July 2004

[3] Dutch Shell website, www.shell.nl

[4] http://www.ecn.nl/_files/bio/Report_2GAVE-03.10.pdf, H. den Uil, *Conventional bio-transportation fuels; an update*, Report 2GAVE-03.10, NOVEM, May 2003, visited: 27 July 2004

[5] http://www.ecn.nl/docs/library/report/2004/c04015.pdf, H. den Uil, R. van Ree, A. van der Drift, H. Boerrigter, *Duurzaam synthesegas: Een brug naar een duurzame energie- en grondstoffenvoorziening*, visited: 27 July 2004

[6] D. Simbeck, H. Johnson, *World Gasification Survey: Industry Trends and Developments,* Paper presented at Gasification Technologies Conference, San Fransisco, October 2001

[7] H. den Uil et al., *Climate neutral transport fuels from biomass; The BIG-FiT concept*, 2002

[8] http://www.novem.nl/default.asp?documentId=115376&preview=ja, K. Kwant, *Conclusions of the Rome World conference on Biofuels (SenterNovem)*, May 2004, visited: 27 July 2004

[9] J.W. Coppelmans, *SUSDAT: A Sustainable Development Analysis tool for the Unit Operations phase of Conceptual Process Design*, Delft University of Technology, Master Graduation Thesis, Delft-The Netherlands, 2004

[10] T.J. Faber, *Development of a Sustainability Assessment Tool for the Early Phases of Chemical Process Design*, Delft University of Technology, Master Graduation Thesis, Delft-The Netherlands, 2004

[11] Delft Design Matrix, Process System Engineering research group, DelftChemTech, Delft University of Technology, http://www.dct.tudelft.nl/pse/ddm/, visited: 26 April-14 May 2004

[12] http://www.webster-dictionary.org/definition/gasification, visited: 27 July 2004

[13] http://www.webster-dictionary.org/definition/biomass, visited: 27 July 2004

[14] J.M. Douglas, *Conceptual Design of Chemical Processes*, McGraw-Hill, 1988

[15] Shell MDS (Malaysia) SDN BHD, *The Shell Middle Distillate Synthesis – Plant at Bintulu*, Shell Malaysia, 1992

[16] Shell Qatar website, www.shell.com/qatar, News and library, *Shell awards design contract for $5 billion Gas to Liquids project to JGC*, 9 March 2004, visited: 20 June 2004

[17] http://www.shellglobalsolutions.com/gasevents/quicklinks/2003_09_Gas_to_Liquids_-_A_paradigm_shift_or_an_opportunity.pdf, A. Brown, *Gas to Liquid – a paradigm shift or a opportunity in the margin?*, 4th International Conference Oil, Gas and Petroleum in Qatar: Opportunities and Developments, September 2003, visited 27 July 2004

[18] http://www.shell.com/static/shellgasandpower-en/downloads/what_is_gas_to_liquids/PwC%, Price Waterhouse Coopers, *Shell*

TUDelft

Middle Distillate Synthesis (SMDS) - Update of a Life Cycle Approach to Assess the Environmental Inputs and Outputs, and Associated Environmental Impacts, of Production and Use of Distillates from a Complex Refinery and SMDS Route, Final LCA report for Shell International Gas Limited, v.3.1. issued on 21 May 2003, visited 27 July 2004

[19] J.M. Smith et al. *Introduction to chemical engineering thermodynamics,* McGraw-Hill, 5th edition, 1996.

[20] http://www.netl.doe.gov/coalpower/gasification/system/shell3x_.pdf, W. Shelton, J. Lyons, Shell Gasifier IGCC Base Cases, NETL, Process Engineering Division, PED-IGCC-98-002, July 1998, revisited in June 2000, visited 27 July 2004

[21] C. Higman, M van der Burgt, *Gasification*, Elsevier, 2003

[22] P. Simell, *Catalytic hot gas cleaning of gasification gas*, Espoo 1997, Technical Research Centre of Finland, VTT Publications 330

[23] P. Simell, *Gasification gas cleaning with nickel monolith catalyst*, A.V. Bridgewater & D.G.B Boocock, Developments in thermodynamic biomass conversion, vol.2, Blackie Academic & Professional, pp. 1103 – 1116

[24] P. Simell, e.a., *Catalytic hot gas cleaning of gasification gas*, Catalysis Today, vol. 27, 55-62, 1996, Elsevier

[25] J.A. Moulijn et al., *Chemical Process Technology*, Wiley, 2001

[26] M.V. Twigg et al., *Catalyst handbook*, London, 2nd ed., 1989

[27] Yumin Li et al., *Study of reactions over sulfide catalysts in CO-CO2-H2-H2O system*, Catalysis Today 51 (1999) 25-38

[28] J.T. Konttinen, C.A.P. Zevenhoven, M.M. Hupa, *Hot gas desulfurization with zinc titanate sorbents in a fluidized bed. 1. Determination of sorbent particle conversion rate model parameters*, Carbona Corporation, Ind. Eng. Chem. Res. 1997, 36, 2332 – 2339

[29] J.T. Konttinen, C.A.P. Zevenhoven, M.M. Hupa, *Hot gas desulfurization with zinc titanate sorbents in a fluidized bed. 2. Reactor model*, Carbona Corporation, Ind. Eng. Chem. Res. 1997, 36, 2332 – 2339

[30] K.C. Kwon, *Kinetics of hot gas desulfurization sorbents for transport reactors*, Annual technical progress report for the period October 1, 2000 to September 20, 2001, DOE, NETL, January 2002

[31] R.A. Newby et al., Novel gas cleaning/conditioning for integrated gasification combined cycle, Based program final report, Siemens Westinghouse Power Corporation & Gas Technology Institute, August 2001

[32] J.T. Konttinen, C.A.P. Zevenhoven, M.M. Hupa, *Modeling of sulfided Zinc Titanate regeneration in a fluidized bed reactor. 2. Scale-up of the solid conversion model*, Carbona Corporation, Ind. Eng. Chem. Res. 1997, 36, 5439 – 5446

[33] http://www.ccee.iastate.edu/courses/ce520/henry.pdf, R. Sander, *Max-Planck Institute of Chemistry, Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry*, visited: 27 July 2004

[34] J.D. Seader and E.J. Henley, *Separation Process Principles*, John Wiley & Sons, 1998

[35] http://www.unece.org/trade/timber/mis/tb-6/tb-56-6.pdf, Timber bulletin, Table 9, visited 27 July 2004

[36] C. Daey Ouwens, G. Küpers, *Lowering the cost of large-scale, biomass based, production of Fischer-Tropsch liquids*

[37] I. Narvaez, e.a., *Fresh tar (from a biomass gasifier) elimination over a commercial steam-reforming catalyst. Kinetics and effect of different variables of operation*, Ind. Eng. Chem. Res., vol. 36, 317-327, 1997, American Chemical Society

[38] E.J. Anthony, R. McCleave, E. Gandolfi, J. Wang, *Industrial-scale demonstration of a new sorbent reactivation technology for fluidized bed combustors*, Journal of Environmental Management, 69, 2003, pg. 177 – 185

[39] R. Meijer, H. Koetzier, A.J.A Konings, L.H.J. Vredenbergt, W.F. van den Broeke, *Unit operations biomass gasification*, Novem, 2DEN-02.20, Utrecht, June 2002

[40] J. Xiao, J. Wei, *Diffusion mechanism of hydrocarbons in zeolite – I. Theory*, Chemical Engineering Science, Vol. 47, No. 5, pp. 1123-1141, 1992

[41] W.J.W. Bakker, L.J.P. van den Broeke, F. Kapteijn, J.A. Moulijn, *Temperature dependence of one component permeation through a silicate-1 membrane*, AIChE Journal, Vol. 43, No. 9, pp. 2203-2214, 1997

[42] A.W. Verkerk, E.L.V. Goetheer, L.J.P. van den Broeke, J.T.F. Keurentjes, *Characteristic of gas permeation through a supported microporous silica membrane*, Journal of Membrane Science (submitted), chapter 3 of Verkerk's promotion thesis, 2002

[43] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Acedemic Publishers, Dordrecht, 2nd edition, 1996

[44] J.C. Diniz da Costa, G.Q. Lu, V. Rudolph, *Permeation of Binary Gas Mixture in Ultramicroporous Membranes*, Journal Nanoscience and Nanotechnology, Vol. 4, No. 3, pp. 265-269, 2004

[45] R. Carapelluci and A. Milazzo, *Membrane system for CO_2 capture and their integration with gas turbine plants*, Journal Power and Energy, Part A, Vol. 217, pp. 505-517, 2003

[46] A. Corti, D. Fiaschi, L. Lombardi, *Carbon dioxide removal in power generation using membrane technology*, Energy, In Press, Corrected Proof, available online at Elsevier Science Direct, 2004

[47] L. Abdellah, B. Boutevin, F. Guida-Pietrasanta, M. Smaihi, *Evaluation of photocrosslinkable fluorinated polydimethylsiloxanes as gas permeation membranes*, Journal of Membrane Science, Vol. 217, pp. 295–298, 2003

[48] J.C. Löttersy, W. Olthuis, P.H. Veltink and P. Bergveld, *The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications*, J. Micromechenical Microengineering, Vol. 7, pp. 145–147, 1997

[49] http://www.cheme.cmu.edu/course/06302/airsep2/index.html, Carnegie Mellon University, Process Design Case Study, visited: 27 July 2004

[50] W.L. Luyben, B.D. Tyréus and M.L. Luyben, *Plant wide process control*, McGraw-Hill, New York, 1999

[51] http://www.ecn.nl/docs/library/report/2004/c04013.pdf, S.V.B. van Paasen, J.H.A. Kiel, *Tar formation in a fluidised-bed gasifier: Impact of fuel properties and operating conditions*, March 2004, visited: 27 July 2004

[52] http://www.gastechnology.org/webroot/downloads/en/IEA/TEriksson.pdf, Foster Wheeler CFB experiences, visited: 27 July 2004

TUDelft

[53] J.M. Coulson, J.F. Richardson, and R.K. Sinnott, *Chemical Engineering -Volume 6: An Introduction to Chemical Engineering Design,* 3rd ed, Butterworth Heinemann

[54] T.E. Lippert et al., *Westinghouse advance particle filter system*, Westinghouse Electric Corporation, Science and technology center, DOE/MC/31147-97/C0714

[55] http://www.netl.doe.gov/publications/proceedings/97/97ps/ps_pdf/PS2A-6.PDF, R.P. Gupta et al., *Desulfurization sorbents for transport-bed applications*, visited: 27 July 2004

[56] http://www.netl.doe.gov/publications/proceedings/01/vision21/v21p.04.pdf, R.V. Siriwardane et al., *Durabel zinc oxide-based regenerable sorbents for desulfurization of syngas in a fixed-bed reactor*, visited: 27 July 2004

[57] http://www.ecn.nl/phyllis/, Phyllis database, ECN website

[58] K.M. Sellakumar, R. Konn, A. Bland, *A comparison study of ACFB and PCFB ash characteristics*, Foster Wheeler Development Corporation and Western Research Institute, 6th International conference on circulating fluidized beds, Wurzburg, Germany, August 22 – 27 1999

[59] http://www.netl.doe.gov/publications/proceedings/00/ubc00/VALER.PDF, M.M Maroto-Valer, et al., *Utilization of unburned carbon from fly ash as precursor for high-value materials*, The Energy Institute, The Pennsylvania State University, visited 27 July 2004

[60] K.M. Sellakumar, R. Konn, A. Bland, *Utilization of CFB fly ash for construction applications*, Foster Wheeler Development Corporation and Western Research Institute, Proceedings of the 15th International conference on fluidized bed combustion, Savannah, Georgia, May 16 – 19 1999

[61] http://www.r-t-o-l.com/modules.php?name=News&file=article&sid=7, refinary technology online site, visited 28 July 2004

[62] http://europa.eu.int/smartapi/cgi/sga_doc?smartapi!celexapi!prod!CELEXnumdoc& lg=en&numdoc=31988L0609&model=guichett, European Union - EuroLex website, visited 28 July 2004

[63] The Dow Chemical Company, *Dow's Fire & Explosion Index Hazard Classification Guide*, the American Institute for Chemical Engineers, New York, 7th edition, 1994

[64] H.J. Pasman and S.M. Lemkowitz, *Chemical Risk Management: safety, health, environmental and sustainability aspects of chemical products and processes*, Delft University of Technology, Faculty of Applied Sciences, Delft, 2003.

[65] http://www.chemeng.ed.ac.uk/~emju49/SP2001/webpage/deh/deh1.html, G. Williamson, *The Dust Explosion Hazard*, 2002, visited: 27 July 2004

[66] Y. Wang, C.M. Kinoshita, *Kinetic model of biomass gasification*, Solar Energy Vol. 51, No. 1, pp. 19–25, 1993

[67] H. Harmsen, KPMG lecture on CO_2 emission trading, KPMG Sustainability, 2004

[68] http://www.ecb.int/stats/monetary/rates/html/index.en.html, European Central Bank website, visited: 28th July 2004

[69] http://www.co2crc.com.au/PUBFILES/PAPERS/Nguyen%20Geological%20Storag e%20Economics%20paper.pdf, G. Allinson and V. Nguyen, CO_2 Geological Storage Economics, School of Petroleum Engineering, University of New South Wales Sydney, Australia, visited: 26th July 2004.

TUDelft