CPD NR 3310

Conceptual Process Design

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

Subject

Design of a process to produce 1000 tonnes per annum of polyhydroxybutyrate (PHB) from waste wood in a Dutch setting.

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Summary

This process is designed to produce 1000 tonnes of PHB (poly hydroxybutyrate) per annum from waste wood. PHB is a biodegradable polymer with similar physical properties to polypropylene, except for a high brittleness.

The current global production of PHB is 500 tonnes per annum. The global production of biodegradable plastics is expected to reach 225,000 tonnes per annum soon. By comparison the total global market for polymers is vast at hundreds of millions of tonnes per annum. PHB currently retails at a price of $12 per kilo. This is close to the price that the process designed achieved (€10 per kilo). The feedstock, waste wood, is readily available at a low price and can be substituted with other biomass sources.

The process achieves production of PHB by gasification of the feedstock, direct fermentation of the gasifier product, syn-gas, to yield intracellular PHB which is then release and purified in a novel downstream process. Gasification is an industrially proven technique. Syn-gas fermentation is still in the experimental phases. The purification process is entirely conceptual, although it is closely related to a process which is in the latter stages of experimental development.

The final design results in a fixed capital cost of €10,138,451 and total investment cost of €11,927,589, this resulted in a DCFROR of 20.5%. The factory starts to work in year 3, the payback time is 6 years. The factory was estimated to be online for 8000 hours per annum, this gives an on-stream factor of 0.91.

Major conclusions are that utilisation of waste biomass as a feedstock is plausible and cost effective. Gasification followed by syn-gas fermentation is a useful technique to achieve the conversion of biomass to useful products and worthy of further consideration. Application of the process at a scale ten times larger would be extremely desirable as this would reduce capital costs dramatically due to the availability of significantly more efficient gasifiers. The total level of uncertainty in the design requires that a number of experiments be conducted. These experiments would be neither complicated nor expensive.

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1 Introduction

1.1 Sustainable processes as a basis for a sustainable society

Our consumer society has a voracious appetite for non-durable products. This leads to large waste streams which often end up polluting the environment and the simultaneous depletion of non-renewable resources. Clearly processes which utilise finite resources to create products which accumulate in the environment are not sustainable in the long term.

Of all materials plastics are possibly the most problematic. Their low cost and the ease with which they are converted into any number of products has resulted in their widespread adoption for single-use applications, such as food packaging. Unfortunately many plastics are often hard to recycle and the process of recycling itself can often consume almost as much energy as producing new plastics.

Within the department of (bio)chemical engineering research is undertaken to develop new processes which approach the problem of supplying societies material needs in a sustainable manner. It is within this context that the current project was undertaken. The objective is to produce an ecologically harmless plastic, polyhydroxybutyrate, from a renewable resource, biomass.

1.2 PHB: A biodegradable polymer

Poly β-hydroxybutyrate (PHB) is in essence a naturally abundant polymer. Many bacteria produce the polymer as a means for energy storage. This implies that the production of PHB does not require the use of fossil fuel feedstocks. Biological feedstocks are well suited for the production of PHB. This makes PHB a potentially sustainable product. The work field of the project owner is lies in sustainability. One of the implementations of sustainability is the idea of chemical highways, and key chemicals to decrease the amounts of reactants used in synthesis.

Polyesters like PHB are biodegradable because the ester bonds can be hydrolysed. Polyesters can be divided into two groups; linear (aliphatic) and aromatic polyesters. The main groups of aliphatic polymers are polybutylene succinate (PBS) polycaprolactone (PCL) polyhydroxyalkanoates (PHA) and polylactic acid (PLA). Only PHAs are naturally produced, but all aliphatic polyesters are biodegradable. PHB is a member of the PHA family, together with polyhydroxyvalerate (PHV) and polyhydroxyhexanoate (PHH). [AG, 2002]

PHB is a very brittle polymer, this disadvantage is somewhat compensated by it’s strength. PHB can be blended with PHV and PHH or produced as a copolymer. The copolymer of PHB and PHV is most common, because the brittleness of PHB is lessened, while its strength is retained. PHB blends with PHH are a relatively new polymer, and it can be used for making mono/multilayer films. Alternatively PHB can also be blended with starch to improve its mechanical properties [Godbole 2003]. The structure of PHB is given in Figure 1-1.

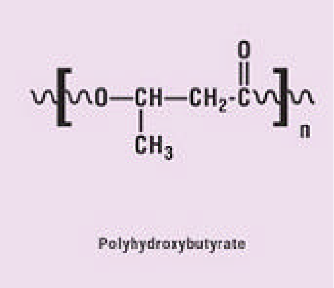


Figure 1-1: The structure of PHB [Icislor 2003]

Biodegradable polymers are mostly used for short-term applications. PLA is commonly used in degradable stitches. Medical application require high purity PHB, because endotoxins resulting from bacterial fermentation can cause inflammation. These purification processes are extremely polluting and in this respect high-purity PLA is much easier to produce.

Other common applications for biodegradable polymers are packings that are not used for long-term storage or sanitary products. A special case of packaging is a biodegradable disposal bag. PHAs only degrade significantly under compostable conditions, typically within weeks. When left in open air or in water, the plastic does not degrade at a considerable rate, typically taking a few years.

The brittleness of pure PHB severely limits the applications of the polymer. Blending or copolymerisation offers many possibilities to widen the range of applications. However, until large-scale processes are cost effective the motivation to research methods for material enhancement is likely to remain small.

1.3 The market for biopolymers

Biodegradable polymers are currently much more expensive than conventional polymers, so in the short-term the application has to be a niche market in order for a process to be profitable. Conventional polymers have a price in the range of €1/kg whereas the price of biodegradable polymers is about €10/kg [AG 2002]. This project group identified application in the production of coffins as a potential application. The market for biodegradable coffins is potentially large enough to sell the volume of plastic produced by this design.

Currently the total market for biodegradable plastics is about 65000 ton/yr [BP 2004]. Most of the biodegradable polymers are starch-based polymers. This market will probably expand to 225000 ton/yr [IBAW 2004]. If PHB represents about 5% of the total market, the current annual world requirement is about 3250 ton/yr [AG 2002]. With the current growth expectations, the demand for PHB will become 14500 ton/yr [ICI 2004].

Therefore the impact of our plant is potentially very large. This is not a problem, because our application does not compete with the other PHB producers. Additionally, we will be the only PHB producing plant in The Netherlands, and the target market was determined to be large enough.

Finally it should be noted that the global production of a typical bulk polymer, such as polypropylene, is measured in tens of millions of tonnes and there are plenty of applications where bioplastics can replace fossil fuel derived materials, so the potential market can be estimated to be five orders of magnitude larger than the our plants output.

1.4 A sustainable process for PHB production

The product, PHB, has to be specified in order to be able to design the process in detail. It was therefore chosen that the main specification is a purity of 95% PHB in the product. Our feedstock, lignocellulosic biomass, can be processed in many ways. A trade-off had to be made between a more hazardous process (gasification) and a large environmentally unfriendly waste stream (acid hydrolysis). The first reaction section was chosen to be gasification because of the relatively neutral waste stream that follows from the process. Waste minimisation was considered to be more important than the hazards introduced by the product gases.

The choice for gasification introduces large uncertainties in the design. Gasification is a very complex process, with many different chemical and physical processes taking place. Simplification was thus necessary. The largest challenge in the design of this unit was to determine which simplifications could be made without seriously deviating from nature. Frequent visits to an expert took the major uncertainties for the design to remain at a high quality. The gasifier of our design has a capacity of 5 MW_{th}.

Fermentation of syn-gas is not a well-known process, so it was very hard to find reliable information in literature. The major uncertainty in the fermentation was the microbiology of the process. The process safety could be ensured by the equipment design and process control structure.

The downstream processing was not really influenced by the choice for gasification followed by direct syn-gas fermentation. The main objective of the downstream processing is to release the product. Within this frame, minimisation of materials consumption and waste production was the major design objective. In the design of the downstream processing a trade-off was made between an unproven concept and the certainty of a large waste stream. After consultation with two experts, the former concept was chosen as the best option.

Considering the innovativity of this design, it is certain no similar plant exists or has been designed. Biomass gasification is usually used for power production, whereas we use the product gas as a feedstock for fermentation. The major drawback of our design is that the numerous uncertainties in the various sub-processes sums to a total process with a large degree of uncertainty. Thankfully each sub process is easy to test independently at the lab-scale.

In order to quantify a design, many data are needed. As is stated above, there were some difficulties finding the necessary information. This lack of knowledge was partly filled by the knowledge obtained from experts, and other information was added by means of educated guesses. Physical data could virtually always be found or estimated from comparable species.

The lifecycle of the process was considered, the results can be found in appendix 1-19.

2 Process options and selection

This chapter outlines the major choices made in the development of a process concept. These are developed into tasks that need to be performed in each sub process.

2.1 PHB synthesis

Theoretically there are two ways to produce PHB from syn-gas, a chemical route and a biological route. However a chemical route is not known. If a chemical route exists at all, research would be needed to find reaction routes and catalysts. This is a time consuming and expensive process, which might not yield any results. The fact that PHB or the monomer 3-β-hydroxybutyrate is a chiral compound complicates the situation, since chiral catalysts are hardly used in the chemical industry and certainly not in the production of bulk polymers.

PHB is a compound that occurs naturally in micro-organisms and plants, except for yeasts and can thus be produced by micro-organisms [Schlegel 1997]. This route has already been the subject of much research, hence micro-organisms can easily be used as miniature PHB factories. A negative aspect of using micro-organisms, in contrast to a chemical route, is the more intensive downstream processing, which results in large waste streams and the formation of by-products.

PHB production is also possible in plants, but they need to be genetically manipulated. A gene is implemented in the plant, which allows the plants to accumulate PHB in its cells. Mosanto has a project that uses plants to produce PHB.

Clearly a fermentative route is currently the only option to produce PHB, since a chemical route is not viable and the use of transgenic plants illegal.

2.2 Choice of feedstock

After analysis of existing PHB production processes it became clear that feedstock costs were a major element in the final price. Several feedstocks were considered, namely: willow, sugar beet, glucose and domestic biodegradable waste (DBW). After careful consideration cutting waste from the fruit industry was chosen as the feedstock. A comparison of the feedstocks is given in appendix 1-1. An important aspect of the decision was the fact that the original assignment of the project owner was to use willow trees. A more detailed rationale behind this decision is explained in appendix 1-1. The choice was partly based on a Piquar evaluation. The raw data of the evaluation are given in appendix 1-2. Piquar is a tool that facilitates decision-making. Its workings are explained in chapter 12.

Table 2-1: Main results of PIQUAR on feedstock

Feedstock	Overall Group score
Willow	6.0
Beet	5.0
Clean left over wood including bark	8.0
Wood cutting from the fruit industry	7.9
DBW	7.5
Glucose	3.9

2.3 Conversion of feedstock to substrate

The first sub-process needs to transform the feedstock to a substrate suitable for bacteria. The two processes evaluated for feedstock conversion were hydrolysis and gasification.

2.3.1 Hydrolysis

Hydrolysis is the chemical depolymerisation of cellulose and hemicellulose to produce a variety of sugars, these are a highly suitable substrate for bacteria. It normally requires treatment of the cellulosic feedstock with concentrated sulphuric acid for 24 hours [Fan 1987]. For the process to be efficient the acid needs to be recovered. Inert elements in the feedstock, such as lignin, remain unconverted. A task structure for hydrolysis is shown in Figure 2-1. More information on hydrolysis is given in appendix 1-4.

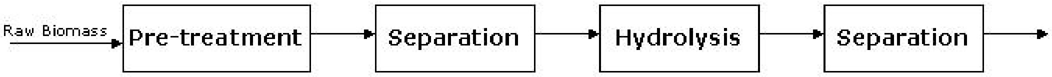


Figure 2-1: Hydrolysis task structure

2.3.2 Gasification

In gasification the biomass feedstock is reacted at high temperature (~1000 ^{o}C) with gases, such as oxygen or steam, to produce primarily hydrogen, carbon monoxide and carbon dioxide. These gases can be converted to a liquid substrate, such as methanol. Another option is to directly feed the syn-gas as a substrate to bacteria that can ferment hydrogen and carbon monoxide [Schlegel 1997].

The task structure for gasification is shown in Figure 2-2.

Figure 2-2: Gasification task structure

Gasification is further explained in appendix 1-5.

Table 2-2 shows a comparison between hydrolysis and gasification according to the Piquar factors as defined by the group. The Piquar values are discussed in appendix 1-6.

Table 2-2: Comparison of hydrolysis and gasification

	Hydrolysis	**Gasification**
Sustainability	0	+
Plant makes money	+	0
Energy, water, space	-	0
Efficient use of raw materials	0	+
Flexibility	0	+
Innovation	-	+
Conversion	0	+
Wastes	-	+

It is clear that gasification has some advantages over hydrolysis. The main problem with hydrolysis is that lignin cannot be converted, leading to a waste stream of approximately 20-30 w-%, depending on the wood type. An advantage is that it is a well-known and rather cheap process and that it yields the best substrate for micro-organisms, namely sugars.

The flexibility advantage of the gasifier is that virtually any carbonaceous feedstock can be converted, including many waste streams. In addition the product, syn-gas, can be used for many other processes (e.g. methanol production). Furthermore, the gasifier almost completely converts the feedstock, so little waste is generated. For these reasons gasification of the feedstock was chosen as the method to produce a substrate suitable for fermentation.

Conversion of syn-gas to a liquid or solid substrate would imply additional cleaning and conversion steps and therefore extra costs. As the syn-gas will be fed to a fermentor, there is no need to remove H_2S and N-containing molecules because bacteria show a higher tolerance to these impurities than ordinary catalysts. According to our criteria syn-gas was determined to be the best choice for a substrate. Appendix 1-7 explains the reasoning behind the choice of substrate in detail.

2.4 Mode of operation

Once the feedstock and substrate have been chosen it has to be decided whether the process should to be operated in batch or continuous mode. Gasification is a continuous process; it cannot be operated in batch mode. On the other hand the fermentation has the possibility to operate in both operation modes. Generally biological reactors are operated in batch to avoid costs associated with the high infection chance. However, in our process the chance for infection is very low because few micro-organisms can grow on syn-gas and most are in fact poisoned by it. Since the storage of syn-gas is potentially dangerous and certainly costly it is wiser to operate continuously. A continuous operation implies lower reactor volumes, a smoother operation and consequently lower investment costs.

2.5 Fermentation process

Since a continuous production process is chosen at least two reaction sections in series are needed for the fermentation. The first section is used for the growth of cells and thus is called the growth section. In the second section the PHB is produced and thus is called the production section.

For both sections the following design aspects should be taken into account

- Choice of the bacterium
- Choice of reactor
- Mass transfer of syn-gas into the reactor
- Mass transfer of oxygen into the reactor
- Heat transfer
- Addition of nutrients

These aspects will be treated further in chapter 5 and 8.
Figure 2-3 gives the steps to perform continuous syn-gas fermentation for PHB production.

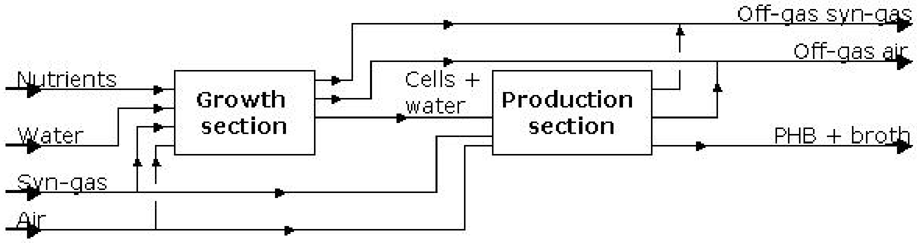


Figure 2-3: Task structure fermentation

2.6 Downstream processing

PHB is an intracellular product, so it has to be removed from the cells. In order to do this, a down-stream processing (DSP) train has been designed. This section explains the various tasks performed by the DSP train.

The function of the DSP sub process is to accept the primary output stream from the fermentation step, the fermentation broth, and produce a stream of PHB which meets the product specification (95% purity). A list of tasks follows from this definition of the sub process objective. These are:

- Cell collection – Separate the cells from the broth liquid.
- PHB release – The cells are lysed (broken open) to make the following separation steps possible.
- PHB recovery – The PHB granules in the suspension are separated from other cell components.
- PHB polishing – PHB is processed further to improve purity and to produce a dry granular product suitable for sale.
- Material recovery – The auxiliary streams introduced during product release are recovered where possible and the waste products are split into streams suitable for further handling.

These tasks are the backbone of every downstream processing section of biotechnological processes. The generic layout of these tasks is illustrated in Figure 2-4.

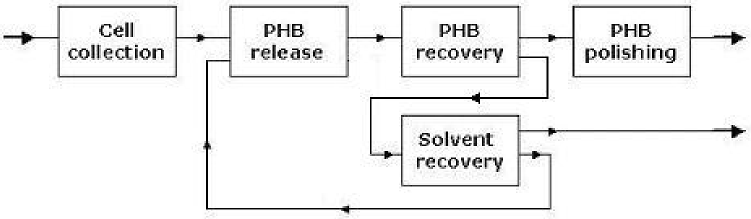


Figure 2-4: Tasks associated with downstream processing

Cell collection is a task that is identical and independent for all processes used for PHB production and is trivial. A number of alternative options exist for the tasks subsequent to cell collection, these are listed below. Each of the options listed below combines the release and purification task, these are the key tasks in the DSP section as they yield the pure PHB product.

- Washing with sodium hypochlorite (NaClO) [Choi 1999]
- Extraction with halogenated organic solvent (generally chloroform) [Ghatnekar 2001]
- Extraction with chloroform and sodium hypochlorite (NaClO) [Ghatnekar 2001]
- Enzymatic release and purification [Scheper 2001]
- Homogenisation with SDS (sodium dodecyl sulphate) solution [Kim 2002, Ling1997]
- Homogenisation with t-butanol solution [Lovrien 1998]

A detailed description of each option and further explanation of the alternatives is found in Appendix 4-1. The last option was chosen, as this was the least polluting, cheapest and extremely fast. It is also the most flexible option as it does not depend so strongly on micro-organism or polymer properties. This makes the process more flexible and robust, this makes it applicable for a wider variety of biopolymer processes.

2.7 Post treatment

In the DSP (downstream processing) sub-process the major objective is the recovery of dry PHB powder with a suitable purity. However the powder obtained consists of particles with a diameter of approximately 600 nm [Ling 1997]. Such particles would be unsuitable for resale for safety reasons (risk of a dust explosion, risk of inhalation). Therefore the final step is to convert the powder in to granules of a few millimetres. A granulator is a standard piece of equipment and the choice of a suitable unit is trivial.

3 Basis of Design (BoD)

3.1 Description of the design

The previous chapters describe how a process concept evolved in accordance with the criteria chosen for the Piquar. In the introduction the nature of the assignment, product and market was described. Chapter 2, process options and selection, showed how the group intended to overcome the challenges identified in the introduction.

The requirement to convert a biomass feedstock in to a substrate suitable for bacterial consumption in a sustainable manner led to the choice for gasification. The ability of certain micro-organisms to directly consume syn-gas made the choice for direct fermentation using syn-gas obvious. Downstream processing, historically an expensive and unsustainable aspect of PHB production, was also approached with the goal of achieving improvements in both critical aspects.

This chapter serves to further define the parameters within which the design is performed, such as feedstock, plant output and location.

The following chapters in this report serve to show how the concepts which have been chosen are translated in to physical units, these are subsequently integrated to optimise the final process. Unit dimensions and stream sizes are calculated and finally the economic performance of the process is accessed to see whether the objectives for the process are achieved.

3.2 Process Definition

This section shows how the decisions made in chapter 2 are integrated to give the complete process. In addition important aspects of the process are described, such as kinetics, stoichiometry and the properties and sizes of the various components and streams in the process.

3.2.1 Process concepts chosen

Wet biomass is gasified in a standard gasification unit using steam and air to produce syn-gas. This is used directly as a substrate for an aerobic fermentation, yielding intracellular PHB. The fermentation uses a system of porous membranes to prevent syn-gas and air mixing to form an explosive gas mixture. In the downstream sub process the intracellular PHB is released and scrubbed clean using a mixture of water and t-butanol (70/30 w-%) to yield 95 w-% pure PHB.

3.2.2 Block schemes

A simple diagram of the process developed in chapter 2 is shown in Figure 3-1.

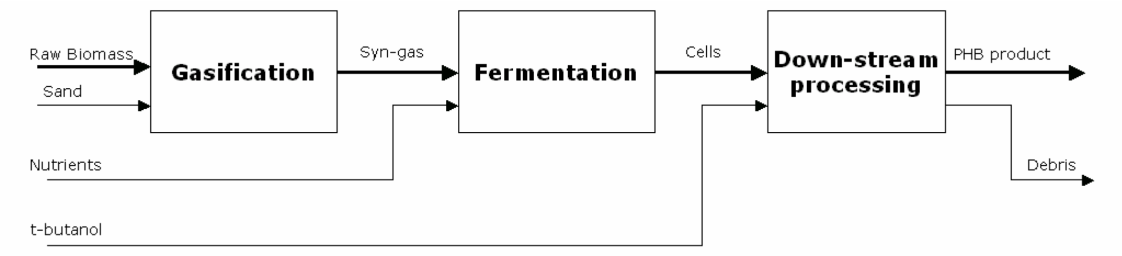


Figure 3-1: Simple process diagram

3.2.3 Thermodynamic properties

A detailed analysis of the three sub-processes shown in Figure 3-1 requires description of the component properties and reaction stoichiometry. For each sub-process a number of important aspects can be highlighted.

Gasifier

In the gasifier a complex network of reactions take place. As gasification is kinetically limited calculations based on thermodynamic equilibrium were only used for the purpose of determining maximum conversions attainable. Accurate prediction of gasifier performance can only be achieved using a kinetic model.

Given the time constraints and the requirement to also devote attention to other aspects of the process it was decided to approach the gasification using a kinetic model which was relatively simple.

Fermentor

In the fermentation sub-process two major modelling issues needed to be addressed. The first issue was the stoichiometry of growth and PHB accumulation. The bacterium used was capable of utilising both CO and H_2 as an energy source and CO and CO_2 as a carbon source. As a result the reaction stoichiometry could vary according which energy sources were more abundant.

As the solubility of both CO and H_2 is low the rate of both growth and PHB accumulation was limited by mass transfer. Additionally varying rates of mass transfer for different gas components resulted in changing gas profiles over the length of the membranes. This reaction system was successfully modelled in Matlab.

Downstream processing

The DSP was characterised by a large dependence on limited empirical information regarding separation performance. The t-butanol stripper utilised a thermodynamic model (NRTL) to determine performance, this showed that the water and t-butanol formed an azeotropic mixture at a water mass fraction of 15 w-%. Calculations regarding heat and work requirements were carried out in Aspen.

3.2.4 Pure component properties

The list of components used in this process is long. For this reason a list of component properties can be found in appendix 1-11 and will not be presented in the main report.

3.3 Basic Assumptions

3.3.1 Plant capacity

The assignment specified a plant capacity of 1000 tonnes PHB per annum. This was the dimension from which all others were derived. Numerous feed and waste streams pass over the battery limit, these are described in the stream summary.

The plant life was taken as 12 years. Plant uptime was assumed to be 8000 hours per annum. This is based on standard assumptions regarding process uptime.

3.3.2 Location

The client stipulated that the process should be developed for a Dutch setting. By locating the PHB-plant near Nijmegen and making agreements with local city governments (Nijmegen, 150,000 inhabitants, Wijchen, 40,000 inh. , Arnhem, 150,000 inh etc.) to obtain part of their green municipal waste, it should be possible to supply the plant with sufficient feedstock.

Additionally, the area between the Maas and the Rijn, a part of Gelderland and Limburg, is a center of fruit farming and thus abundant in cuttings from this industry. Trees are pruned in the summer and in the winter, the fruit industry alone generates 294,000 tonnes of wood waste a year, of which 100,000 tonnes are not currently utilised [TNO 2001]. By comparison it was estimated that the process would require 12,400 tonnes of wood waste per annum.

3.3.3 Battery limit

The battery limit was taken as the limits of the process plant. Detailed engineering calculations were only carried out for the elements of the product lifecycle from feedstock preparation up to and including PHB granule storage. This was the area within which the groups expertise was strongest.

3.4 Definition In- and Outgoing streams & Economic Margin

Table 3-1 and Table 3-2 show all stream crossing the system boundary. In addition streams costs and utilities are given. A description of each stream can be found in Table 3-1.

Table 3-1: **Description of streams**

Stream **Incoming streams**	**Numbers**	**Description**
Wood feed	<1>	Raw feedstock for process
Air feed	<37><39>	Air needed for fermentation and gasification
T-butanol	<78>	T-butanol makeup for the DSP
Sand	<34>	Makeup sand for fluid bed, sand is lost with the ashes
Nutrients	<53>	Nutrients required for the fermentation
Outgoing streams		
PHB	<33>	Product
Syn-gas	<76>	Unconverted syn-gas
Air	<77>	Used air
Water	<52><95>	Waste water
Ash	<47><48>	Ash from gasifier

Table 3-2: In- and Outgoing streams and economic margin

Stream	Size [tonne/yr]	Price [€/unit]	Cost [€/yr]
Incoming streams			
Wood feed	12,400	13	161,200
Air feed	92,736	0	0
T-butanol	5	1,250	6,250
Sand	12	20	240
Nutrients	134	245	32,830
Outgoing streams			
PHB	1,008	-10,000	-10,080,000
Syn-gas	12,931.2	0	0
Air	87,810.8	0	0
Water	12,009.6	0.1	1,201
Ash	56	0	0
Economic margin			-9,878,279
Utilities			
Water feed [tonne/yr]	8,352	0.1	835
Electricity [KWH/yr]	7,413,639	0.12	889,637
Methane [tonne/yr]	5.3	357	1,892
Total utilities cost			892,364

These values lead to a maximal fixed capital cost of €12,470,295 and total investment cost of €14,670,935 for a Discount Cash Flow Rate Of Return (DCFROR) of 10%. In the final process a fixed capital cost of €10,138,451 and total investment cost of €11,927,589 were found, this resulted in a DCFROR of 20.5%.

4 Thermodynamics and reaction kinetics

In this chapter the stoichiometry and thermodynamics of each sub process are discussed. In addition general comments regarding calculation methods employed are presented. This chapter therefore serves to familiarise the reader with the methods employed and the assumptions made during calculations. The three sub-processes, gasification, fermentation and downstream processing are treated in the order they occur in the process.

4.1 Gasification thermodynamics and kinetics

Gasification is a very complex process. It can be divided into two reaction types: wood pyrolysis and gasification. This section describes the thermodynamics and the kinetic considerations of this reaction system.

One of the first calculations that need to be done in order to determine the kinetics of gasification is to clarify the stoichiometry of the different reactions that take place. In order to do this, the molecular formulae of all components needed to be determined.

The following components are important in gasification:
Biomass ($C_{42}H_{60}O_{28}$), carbon dioxide (CO_2), carbon monoxide (CO), char ($C_{16}H_{10}O_2$), hydrogen (H_2), methane (CH_4), oxygen (O_2), tar ($C_{28}H_{34}O_9$), water (H_2O).

4.1.1 Pyrolysis kinetics

Upon entering the gasifier, the feed is completely converted into char, tar and gases.
The overall pyrolysis reaction is as follows:

$$C_{42}H_{60}O_{28} \rightarrow aCO + bCO_2 + cH_2O + dH_2 + eC_{16}H_{10}O_2 + fC_{28}H_{34}O_9$$

The actual values depend on the conditions, primarily temperature and pressure, in the gasifier. For the conditions chosen for this gasifier the coefficients are given in Table 4-1.

Table 4-1. Stoichiometric coefficients for pyrolysis reactions at given conditions

Coefficient	value	Coefficient	value
a	1.39	**d**	1.39
b	3.30	**e**	1.30
c	12.08	**f**	0.59

The calculation of the coefficients in given in appendix 3-1.

Pyrolysis actually consists of a complex system of reactions. There are 5 reactions taking place, which are given in Figure 4-1.

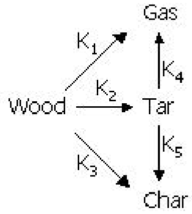


Figure 4-1: Reaction scheme for wood pyrolysis. Adapted from Mousques [2001]

For further calculations, the molecular formula of char is assumed to be C. This is a common assumption in gasification and is based on the carbon content in char. The relative elemental distribution is 82% carbon, 4% hydrogen, and 14% oxygen. This justifies the assumption of modelling char as elemental carbon.

All reactions are first-order, the kinetic equations are given below.

$$r_1 = k_0 \exp\left(-\frac{E_{A,1}}{RT}\right) C_{Wood}$$

$$r_2 = k_0 \exp\left(-\frac{E_{A,2}}{RT}\right) C_{Wood}$$

$$r_3 = k_0 \exp\left(-\frac{E_{A,3}}{RT}\right) C_{Wood}$$

$$r_4 = k_0 \exp\left(-\frac{E_{A,4}}{RT}\right) C_{Tar}$$

$$r_5 = k_0 \exp\left(-\frac{E_{A,5}}{RT}\right) C_{Tar}$$

The accompanying kinetic parameters for these reactions are given in Table 4-2. The heats of reaction are given at 800 ºC. The gasifier is run at 1000 ºC, so therefore the introduced error is acceptable.

Table 4-2. Kinetic parameters for pyrolysis. Adapted from Mousques [2001]

	k_0 [s^{-1}]	**E_A [$^J/_{mol}$]**	D_r**H** [$^{kJ}/_{kg}$]
K_1	$1.43 \cdot 10^4$	$8.86.10^4$	418
K_2	$4.13 \cdot 10^6$	$1.127 \cdot 10^5$	418
K_3	$7.38 \cdot 10^5$	$1.065 \cdot 10^5$	418
K_4	$4.28 \cdot 10^6$	$1.08 \cdot 10^5$	-42
K_5	10^5	$1.08 \cdot 10^5$	-42

4.1.2 Gasification kinetics

It was found in the literature [Moulijn 2001; De Jong 2003; Van Aarsen 1985] that the following reactions are most important in the modelling of gasification of char:
The reactions for the gasification of char were given to be:

$$1. C_{28}H_{34}O_9 \rightarrow 9CO + 8.5CH_4 + 10.5C$$

$$2. C + O_2 \rightarrow CO_2$$

$$3. C + H_2O \rightarrow CO + H_2$$

$$4. C + CO_2 \rightarrow 2CO$$

$$5. C + 2H_2 \rightarrow CH_4$$

$$6. CO + H_2O \rightarrow CO_2 + H_2$$

$$7. CH_4 + \frac{3}{2}O_2 \rightarrow CO + H_2O$$

The kinetic equations for these reactions are as follows [Bruch 2003; De Jong 2003]:

$$r_1 = k_0 \exp\left(-\frac{E_{A,1}}{RT}\right) C_{tar}$$

$$r_2 = k_0 \exp\left(-\frac{E_{A,2}}{RT}\right) C_{O_2}$$

$$r_3 = k_0 S \exp\left(-\frac{E_{A,3}}{RT}\right) C_{H_2O}^{0.83} \left(1000\right)^{-0.17} e_c$$

$$r_4 = k_0 S \exp\left(-\frac{E_{A,4}}{RT}\right) C_{CO_2}^{0.83} \left(1000\right)^{-0.17} e_c$$

$$r_5 = k_0 S \exp\left(-\frac{E_{A,5}}{RT}\right) C_{H_2} e_c$$

$$r_6 = k_0 \exp\left(-\frac{E_{A,6}}{RT}\right) \left[C_{CO} C_{H_2O} - \frac{C_{H_2} C_{CO_2}}{k_{eq}} \right] e_c$$

$$k_{eq} = \exp\left(-\frac{65800}{RT}\right)$$

$$r_7 = k_0 \exp\left(-\frac{E_{A,7}}{RT}\right) C_{CH_4} C_{O_2}$$

The kinetic parameters for these reactions are given in Table 4-3.

Table 4-3. Kinetic parameters for gasification. [Hamel 2001; Prins 2003]

	k_0 [s^{-1}]	E_A [$^J/_{mol}$]	D_rH [$^{kJ}/_{kg}$]
K_1	$3.7 \cdot 10^7$	$1.18 \cdot 10^5$	418
K_2	301	$1.49 \cdot 10^5$	-395
K_3	14.4	$1.66 \cdot 10^5$	135.8
K_4	7.2	$1.66 \cdot 10^5$	169.8
K_5	$2.7 \cdot 10^7$	$2.30 \cdot 10^5$	-34
K_6	2.78	$0.126 \cdot 10^5$	-42
K_7	$2.79 \cdot 10^8$	$1.31 \cdot 10^5$	-8310.4

The *S* in the kinetics stands for specific surface. The powers that occur in the second and third reactions are incorporated to account for mass transfer limitations in the fluidised bed. The kinetic data are valid in the range of operation.

4.2 Fermentation

In the fermentors numerous physical processes take place. Syn-gas diffuses through the pores of the membranes, gases absorb and desorb between the gas and liquid phases, dissolved gases are consumed and produced by the bacteria. Clearly these phenomena require various models to describe the rate and extent at which they take place.

In this part the (thermochemical) data used in the fermentation sub process as well as the reaction stoichiometry will be discussed. The data required can be divided in two parts, namely data relating to the broth and data needed for the gas phases. The thermodynamics of the broth and gas phases will be discussed first followed by the stoichiometry. All calculations regarding the fermentor are carried out using the assumption that it operates at 40 ^oC.

4.2.1 Data relating to the broth

The density and viscosity of the broth are assumed to be equal to that of water of 298 K and constant with temperature. Both are given in Table 4-4 [Jansen 1997].

For the heat balance calculations the amount of water is needed which vaporises to the gas phase. This will be calculated with Raoult's law [Smith and Van Ness 2002]. For this law the vapour pressure of water is needed at the reactor temperature, which will be calculated with the Antoine equations. A further data requirement to solve the heat balances is the heat capacity of the broth. This heat capacity is also assumed to be equal to that of water. Both are given in Table 4-4.

Table 4-4: Required data on the broth [Webbook 2004]

4.2.2 Property	Value	Units
Density	1000	kg/m^3
Viscosity	0.001	kg/m·s^2
Vapor pressure at 40 ^oC	7407	Pa
Heat capacity of water at 20 ^oC	75.6	J/(mol·K)
Heat capacity of water at 40 ^oC	75.3	J/(mol·K)

4.2.3 Data for the gas phases

In order to calculate the solubilities of the different gas components in syn-gas and air Henry's law is used. The Henry constants at the reactor temperature are given in Table 4-5. The fermentation is isothermal, so the data are valid for the operating conditions.

Table 4-5: Henry constant at the reactor temperature (40 ^0C) [SWBIC 1998]

	$k_{H,inv}^{cc}$	Units
H_2	55.47	[-]
CO	51.41	[-]
CO_2	1.721	[-]
O_2	39.52	[-]
N_2	76.82	[-]

Henry constants are used and given with different dimensions throughout the literature. In order to convert the Henry constants to other dimensions a Henry constant converter was used [Sander 2001].

The diffusivities of the gas components in the liquid are also required to model the gas-liquid mass transfer. Liquid diffusivities for the reactor temperature are listed in Table 4-6. The diffusivities of hydrogen and carbon dioxide at the reactor temperature are calculated by linear interpolation of the values obtained at different temperatures [Lide 2000]. Considering the small temperature range (10 to 35 ºC) and the high least square sum (0.997 for hydrogen, 0.995 for carbon monoxide and 0.997 for oxygen) this linearisation is expected to give reasonable values. The liquid diffusivities of nitrogen and carbon monoxide at reactor temperature were calculated with the Wilke and Chang relation for liquid diffusivities.

Table 4-6: Liquid diffusivities of the gas components at 40 °C [Sinnot 2000]

	Δ_{liquid}	4.2.4 Units
H_2	$5.70 \cdot 10^{-9}$	$[m^2/s]$
CO	$1.83 \cdot 10^{-9}$	$[m^2/s]$
CO_2	$2.10 \cdot 10^{-9}$	$[m^2/s]$
O_2	$3.91 \cdot 10^{-9}$	$[m^2/s]$
N_2	$1.81 \cdot 10^{-9}$	$[m^2/s]$

As will be discussed in chapter 5, silicon rubber membranes will be used for the transfer of the syn-gas to the liquid phase. This requires the membrane permeabilities of the syn-gas components. The permeabilities are given in Table 4-7 at 20 °C. Permeabilities at other temperatures are however not available, thus it will be assumed that the permeability is reasonably constant over the used temperature range.

Table 4-7: Permeability of syn-gas components through silicon rubber membranes at 20°C [Geankoplis 2003]

	P_m	4.2.5 Units
H_2	$171 \cdot 10^{-15}$	$[mol/(s \cdot m \cdot Pa)]$
CO	$9.33 \cdot 10^{-15}$	$[mol/(s \cdot m \cdot Pa)]$
CO_2	$839 \cdot 10^{-15}$	$[mol/(s \cdot m \cdot Pa)]$
N_2	$7.77 \cdot 10^{-15}$	$[mol/(s \cdot m \cdot Pa)]$

For the calculations concerning the heat balances the specific heats of the gas components at incoming and reaction temperature are required. The produced syn-gas is cooled down to the temperature of the reactor and thus within the fermentor the temperature and hence the specific heat values do not change. However the incoming air temperature is 20 °C. The values of the specific heats are given in Table 4-8. Since syn-gas enters the fermentor at 40 °C, the heat capacities of its components at 20 °C are not relevant and therefore not included.

Table 4-8: Heat capacities of the gas components at reactor temperature and incoming temperature [Webbook 2004].

		20 °C	40 °C	4.2.6 Units
H_2	C_p	n.r.	28.9	$[J/(mol \cdot K)]$
CO	C_p	n.r.	29.1	$[J/(mol \cdot K)]$
O_2	C_p	28.8	29.2	$[J/(mol \cdot K)]$
CO_2	C_p	n.r.	37.8	$[J/(mol \cdot K)]$
N_2	C_p	28.8	28.9	$[J/(mol \cdot K)]$

4.2.7 Stoichiometry

Two stoichiometries are used in modelling the fermentation. The stoichiometry of growth is used for the growth reactor and the stoichiometry for PHB production is used for the production reactor. The stoichiometry is briefly described below, a thorough discussion can be found in appendix 2-1.

4.2.8 Growth reaction

Biomass is built up from hydrogen, oxygen and carbon monoxide [Schlegel 1961]. For the production of 1 C-mole of biomass at least 1 mole of hydrogen needs to be fixated as well as 1 mole carbon monoxide or carbon dioxide. Hydrogen and carbon monoxide are also energy sources for the bacteria and both deliver approximately the same amount of energy [Schlegel 1997]. For the production of 1 C-mole of biomass 6 energy equivalents (cumulative moles of hydrogen and carbon monoxide) are required [Schlegel 1997].

The bacteria will consume all the hydrogen and carbon monoxide transferred, since the reaction rate is mass transfer limited. This means the stoichiometry is a function of the ratio of the transferred hydrogen and carbon monoxide. This ratio will be defined as the transferred hydrogen divided by the transferred carbon monoxide. This will give the following stoichiometry:

$$\frac{6\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}H_2 + 2O_2 + \frac{6}{1+TR_{H_2/CO}}CO \rightarrow <CH_2O> + \frac{5\cdot TR_{H_2/CO}-1}{1+TR_{H_2/CO}}H_2O + \frac{5-TR_{H_2/CO}}{1+TR_{H_2/CO}}CO_2$$

$TR_{H2/CO}$ represents the transfer ratio and $<CH_2O>$ 1 C-mole of biomass. The ratio can vary from 0.2 till infinity, since one hydrogen molecule has to be fixed into the biomass. Note that if the transfer ratio is greater than 5 carbon dioxide will be consumed in order to be able to fixate enough carbon.

4.2.9 PHB production reaction

PHB is also built up from hydrogen, oxygen and carbon monoxide. For the production of 1 mole of dehydrated PHB monomer 3 moles of hydrogen need to be fixed as well as 4 moles of carbon monoxide [Schlegel 1961]. For the production of 1 mole of dehydrated PHB monomer 25 energy equivalents are necessary. As in the growth reaction the PHB production stoichiometry is also dependent on the ratio of hydrogen and carbon monoxide transfer. This will give the following stoichiometry for PHB production:

$$\frac{25\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}H_2 + 8O_2 + \frac{25}{1+TR_{H_2/CO}}CO \rightarrow -\left[C_4H_6O_2\right]- + \frac{22\cdot TR_{H_2/CO}-3}{1+TR_{H_2/CO}}H_2O + \frac{21-4\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}CO_2$$

In which $–[C_4H_6O_2]-$ represents the dehydrated PHB monomer. In which the ratio can vary from 0.14 to infinity, since three hydrogen molecules have to be fixed into the PHB. Note that if the transfer ratio is larger than 5.25 carbon dioxide will be net consumed as a carbon source.

4.3 Downstream processing

Within the downstream processing section no chemical reactions take place. However a large number of equilibria between are used to achieve purification. Modelling these equilibria is often impossible using normal thermodynamic methods as the components are poorly defined. For instance ‘cell debris’ is a major impurity and will consist of thousands of components with the composition varying per fermentation.

For this reason many calculations performed during development of the DSP sub-process were based on experimental values found in the literature. In order to perform the necessary calculations the following data were collected:

Table 4-9: Properties used for DSP calculation. [Kim 2002; Ghatnekar 2002; Ling 1997]

4.3.1 Property	Value	Unit
Density of PHB ?$_{PHB}$	1250	kg/m^3
Density of t-butanol ?$_b$	800	kg/m^3
Water content in PHB-free biomass X$_{C,w}$	0.75	g/g
Optimal fraction SDS in a homogeniser solution	5	w-%
Optimal fraction of t-butanol in a homogeniser solution	30	w-%
Solvation capacity of SDS	0.72	g SDS/g cell debris
Viscosity of the fermentor broth	$1.2\cdot10^{-3}$	Pa·s

A value for the solvation capacity of t-butanol had to be estimated as 0.12. A certain number of logical assumptions had to be applied to arrive at an estimate. Firstly it was assumed that an identical quantity of 30 w-% t-butanol solution and 5 w-% SDS solution would be capable of solvating an equal quantity of debris. This assumption is equivalent to saying that t-butanol is six times less effective in solvating debris than SDS, on a mass basis. This is likely to be a conservative estimate, experiments would need to be carried out to determine what the real capability of t-butanol is for this application.

The TXY phase diagram for t-butanol and water is given in appendix 4-6. The mixture forms an azeotrope at a water mass fraction of 15 w-%. Clearly it is not possible to recover pure t-butanol with one column, however this is not a design objective. The objective is to have as little t-butanol in the bottom stream of the stripper, this is achievable.

5 Process structure, description and yields

In this chapter specific units are chosen to perform the tasks identified in chapter 2. Once appropriate units are chosen the connectivity between these units is formalised in a process flow sheet, which is described in the second part.

5.1 Criteria and selections

5.1.1 Pre-treatment

The feed that enters the plant usually needs to be adjusted to the specific needs of the processing units that follow. Some processes have very specific input specifications and need extensive pre-treatment of the feed.

Gasifiers normally require a highly specified feedstock, but the pre-treatment of the current process is very simple since the chosen gasifier can handle a wide variety of feedstock types, so pre-treatment is largely unnecessary. This consists only of size reduction, because smaller particles yield better results in the gasifier. If the biomass feedstock were too wet then drying might become necessary, this is not the case for the waste wood feedstock chosen.

Biomass particles (1550 kg/hr) enter the factory as chips with a (surface-volume sphere) diameter of approximately 2 cm and a moisture content of 25 w-%. They could be washed first, but it is assumed that they are not very dirty and therefore this step is not necessary.

Breaking down the particles is a very energy intensive process, so a trade-off needs to be made between particle size and cost. The particles have to be fluidised, so the admissible size is within a narrow range. The balance was found in biomass particles of 5 mm. This is a typical particle size for a fluidised bed [Moulijn 2001]. Therefore the particle size has to be reduced.

5.1.2 Gasification

Many different possible reactors were found for the gasification step. Appendix 3-2 discussed various types of reactors. Some are single step reactors, some are multiple step reactors [Rudloff 2003; Milne 1998; ECN 2004; Moulijn et al. 2001; NREL 2003; Tomishige 2004; Palonen 1999; Rüdiger 1997].
The next table gives a comparison of the different possible reactors that could be used.

Table 5-1 Selecting a gasifier design [Seghers Keppel; Lurgi Methanol-to-Power, 2004; Zevenhoven, 2000; Babu, 1999; ECN, 2001; CSIRO, 2004; Moulijn, 2001, De Jong, 2004]

	Type	O_2 consumption [kg/kg feed]	$T_{reactor}$ [K]	T_{exit} [K]	Pressure [bar]
Lurgi	Moving bed	0.5	1250-1350	700	1
Winkler	Fluidised bed	0.7	1250-1400	1150	1-20
FBR	Fluidised bed	0.4	1250-1400	1150	1-20
CFB	Fluidised bed		1200-1600		1
Entrained flow	Entrained flow	0.9	1600-2200	1300	1-40
Silva	Fluidised bed		1150-1300		
Carbo-V	Combination		1000-1800		1

Table 5-2 continued

	LHV [MJ/kg]	HHV [MJ/Nm^3]	Feed [ton/hr]	D_p [mm]	Thermal Efficiency [%]	Thermal Energy Raise capacity
Lurgi	10-20		13-62	20-35	70-80	10
Winkler		6-12	125		50	
FBR	18		10	2	36	5.5-100
CFB			7	<50	56	10-500
Entrained flow			>200	<0.1	50	>500
Silva		18	10		82	
Carbo-V	5-9		10-99		80	

During our conversation with an expert, ir. De Jong, it became clear that for a small plant like this (± 5MW) a fluidised bed is the best cost-effective option, furthermore it is a relatively simple design. A discussion of the visit in given in appendix 8-1. For these reasons the normal fluidised bed (FBR) has been selected. This type of reactor is optimal for achieving the process specifications.

The reactor is fed with air and steam. It is operated at a pressure of 5 bar and at a temperature of 1273 K. Air was chosen as pure oxygen is too expensive for a small reactor. [Pletka 1998; Moulijn 2001] Air is used to provide energy for the endothermic gasification, the reaction of the carbon with oxygen is exothermic. To prevent complete combustion only 1/3 of the stoichiometric ratio of oxygen is fed. Steam is used to obtain a more reducing environment and to promote the water-gas shift in order to obtain a higher H_2:CO ratio. High hydrogen to carbon monoxide ratio is required for high feedstock conversion in the fermentation section.

Of the contents of the gasifier only 2 vol-% is wood, the balance is sand.

The FBR has a grid in the bottom to remove non-fluidisable particles, predominantly ashes. The exit stream at the top is composed of H_2, CO, CO_2, N_2, water, a little tar and fly-ash. This stream is led through a cyclone, followed by a ceramic filter and a heat exchanger. Water has to be removed from the exit stream. This is done by a gas-liquid separator. After cooling, syn-gas containing nitrogen is fed to the fermentor (T = 40ºC, p=5 bar).

The filter could be a bag-filter or a ceramic filter. The advantage of the ceramic filter is that it can easily handle tar, by periodically burning off this sticky substance. If a bag-filter had been used, tar would need to be removed in a scrubber first. A bag-filter would be cheaper, but at least one extra unit would be needed.

For the calculation of the syn-gas composition that leaves the gasifier, the data from Aspen are used, due to unreliable results from the kinetic calculations.

5.1.3 Fermentation

Continuous operation forces the construction of two separate reaction sections; one for the growth of the micro-organisms (the growth reactor), and a second for the production of PHB (the production reactor).

Both reactors are fed with syn-gas, oxygen and water. The microorganism used is said to grow with the same characteristics as Alcaligenes Eutrophus (see appendix 2-1). These types of microorganisms are able to produce PHB from a wide variety of substrates

Gases constitute the feed or substrate of the micro-organisms. Micro-organisms are only able to grow in liquid or highly hydrated media. Therefore the gaseous substrate needs to be absorbed prior to consumption by the bacteria. Hence the reactor also has to guarantee high mass transfer rates to reach acceptable conversion rates.

An aerobic fermentation will be performed since aerobic conversion of syn-gas into poly-hydroxybutyrate gives higher yields compared to anaerobic fermentation [Schlegel 1997]. Air is used instead of oxygen for oxygen supply, because pure oxygen is expensive and would increase operating costs of the process. Moreover the solubility of hydrogen and carbon monoxide is much lower than oxygen and mass transfer of those gases and not that of oxygen will be rate limiting. Oxygen has a higher solubility so the reactor dimensions are mainly determined by the mass transfer rates of carbon monoxide and hydrogen.

The reactors have to fulfil safety requirements, this means minimising explosion risks (because of the presence of hydrogen and oxygen in the same reaction) and maximising conversion of syn-gas into PHB.

According to these requirements some reactor types and configurations are proposed (bubble column, bubble columns in series, membrane aerated bioreactor, monolith reactor and CSTR with micro-bubbles). These are further explained in appendix 2-2.

The main reason for choosing the membrane bioreactor was the possibility to contact the two gases (air and syn-gas) separately with the liquid phase and the possibility of choosing the mass transfer contacting area.

Because all hydrogen and carbon monoxide that passes through the membranes is rapidly consumed by the microorganisms the explosion risk is strongly reduced. Therefore hydrogen and oxygen can hardly mix to form explosive mixtures. The alternative reactor configurations didn't give this possibility.

The membranes are made of silicone rubber, and are open-ended membranes (since sealed end membranes are less effective and not appropriate for industrial scale aeration) [Tariq Ahmed 1995]. Silicone rubber membranes are strong, can withstand large pressure differences (7 bar) and possess a high permeability for gases. [Geankoplis 2003]. This makes silicone rubber membranes highly appropriate for this application.

Because membranes are quite expensive, it was decided to introduce the syn-gas through the membranes and the air by means of gas bubbles instead of through the membranes. Besides reducing costs, because less membrane surface is required, this option also contributes to a high degree of mixing and thereby avoiding bio-film formation (fouling) on the membrane surface.

To achieve a narrower residence time distribution of the cells in the system the production reaction section is split in to three reactors in series. This also allows for safer operation because in the event of a critical failure less gas is present in the reactor. It also gives the possibility to shut down one of the reactors while keeping the others online.

The pressure in the reactor will be 5 bar and that of the syn-gas 10 bar; a mild pressure difference considerably increases the solubility of gases in liquids and therefore reduces the required membrane surface. The temperature in the reactor is chosen to be 40°C since this temperature is quite common in the bioprocess technology. At higher temperatures the solubility of gases decreases and the chance of protein denaturation increases to its limits, in the other hand when the temperature is too low, the microbial activity decreases.

Because the cell concentration in the reactor is chosen to be high, it is expected that this aspect will reduce separation costs in the down stream process, particularly in the micro-filtration section.

The mass balances and design equations are clarified in appendix 2-3.

5.1.4 Downstream Processing

As explained in chapter 2 and appendices 4-2 and 4-3 the DSP sub process achieves PHB release and polishing by means of homogenisation with 30/70 t-butanol/water solution. The block scheme with the tasks is given in appendix 1-17.

Cell collection

The first step in the down-stream sub process is to separate the bacteria from the broth. Two options were suitable for this step, centrifugation and micro-filtration. Micro-filtration appeared to be the best technique for the following reasons.

The broth is a very heterogeneous mixture of various components and it is difficult to classify all these components. In this step the main purpose is to remove the cells from the broth. If this would be done by centrifugation, there is a chance that there are components in the broth that behave like the cells in terms of sedimentation rate. This is less likely to occur in micro-filtration where size is the distinguishing characteristic.

A second consideration is the economics of the process. Micro-filtration is generally speaking cheaper and less energy intensive than centrifugation. When the particles to be separated are of a sufficient diameter then the pore size in the membrane can be so large that a significant permeate flux can be achieved with modest pressure. During centrifugation is that there is also a chance that bacterial cells are destroyed by the shear stress in the centrifuge, which may cause the yield of PHB to decrease. Another advantage of micro-filtration over centrifugation is the time needed to accomplish the separation. [Biodata 2002]

Release and purification of PHB granules

Having collected the cells, the next step is to release the PHB granules from them. The two tasks of releasing the PHB granules and purifying them are combined in all process concepts considered for DSP. Homogenisation, the technique chosen for these tasks, is the process of forcing a cell suspension through a narrow orifice. This generates massive shear stresses that cause the cells to rupture. In essence the homogeniser is a pump followed by a valve. Because of the high pressures required, a reciprocal pump is the only suitable choice. A ceramic valve was chosen because the higher mechanical strength enables longer continuous operation.

PHB recovery

PHB recovery is a similar task to cell collection, because micron scale particles (~0.6 microns [Lee 1997]) are separated from a liquid suspension. There are however a number of significant differences between the two streams. Firstly the PHB granules are significantly denser than the cells, this makes a density sensitive method particularly effective. In addition the PHB granules have a diameter of approximately 0.6 microns compared to a diameter of 1.5 microns for the cells [Ling 1997]. This would mean the pore size in a micro-filtration unit would have to be significantly smaller, making micro-filtration more energy intensive and the membrane more expensive. Numerous authors have reported high granule yields under moderate centrifugation [Ghatnekar 2002, de Koning 1997]. For these reasons a centrifuge was chosen.

A variety of centrifuge configurations are available, however for the particle and stream size under consideration only a disk centrifuge was suitable. Due to the continuous nature of the process it was decided to use a disk centrifuge with continuous discharge through a nozzle. [Harrison 2003]

PHB Polishing

The raw product stream exiting the first disk centrifuge still contains a significant quantity of impurities. Therefore the next operation is to re-suspend the impure PHB granules in a clean liquid. In addition the end product should be dry PHB granules, hence a final drying step is also required.

Centrifugation is the obvious choice for wet product recovery for the same reasons given for raw PHB recovery. The PHB sediment passes to the drier and the clarified, t-butanol rich liquid is recycled to the beginning of the sub-process.

Drying

For this step the vapour from the top of the stripper (see solvent recovery) and the condensed stream of clean granules are combined to form an aerosol spray. This causes any remaining solvent to evaporate, resulting in a dry product. The dry granules are recovered from the vapour stream using a cyclone. This is possible because polymer particles quickly become statically charged and agglomerate. The vapour leaving the drier is then led back to the polishing step via a condenser, in this way any PHB granules not removed in the cyclone will remain inside the polishing section of the sub-process.

Solvent recovery

The liquid stream leaving the raw PHB recovery step contains all the non-PHB cell material (NPCM), this needs to be removed. In addition water introduced in to the DSP sub-process dilutes the solvent, hence it is necessary to remove water not separated in the micro-filtration unit. The objective of these two steps is therefore to regenerate the solvent.

The solvent recovery was another task for which many units were synthesised. The various syntheses are listed and explained in Appendix 4-3. After considering each alternative on it's merits the use of a stripper was clearly the best option.

In the stripper steam is contacted counter-currently with the impure solvent. This strips the t-butanol from the liquid in to the vapour. As the temperature increases and t-butanol is removed the solvating capabilities of the liquid for cell debris will decrease, this causes the debris to precipitate. As a result the liquid stream leaving the bottom of the stripper contains virtually no t-butanol and will contain particulate cell debris of a size suitable for removal.

Debris removal

The debris in the water stream leaving the bottom of the stripper should be removed, this is because part of the water needs to be recycled within the DSP sub-process. To achieve removal of debris to the micron level the choice of unit would be between a centrifuge and a micro-filtration unit. A micro-filtration unit could easily become fouled, which would lead to diminishing unit performance. For this reason a centrifuge was chosen.

5.2 Process flow scheme (PFS)

5.2.1 Gasification

Wood is led to a grinder, after which two hoppers pressurise the biomass particles. The air <37>that enters the system is compressed and then split. By using this configuration, only one compressor (K02) is needed to pressurise all air that is needed in the process. Pressurised air <40> is heat exchanged with the gasifier effluent and then led into the gasifier (R01). Steam <46> for the gasification is produced by heat exchange with the gasification effluent <6>. The gasification effluent is heat exchanged three times in total. First the air and water are heated to reaction temperature, and then steam for the stripper in the downstream processing is produced. After heat exchange, the gas flow <8> is led through a cyclone (S01) in order to remove fly ash. The effluent <9> is sent through a filter (S02). Tar deposits on the filter, which introduces the need for periodical cleaning. The clean gas <10> is cooled (E06) and then flashed (V03) in order to remove water. A constant water purge <52> is introduced to keep the amount of inerts at a constant level. The dried syn-gas <11> is pressurised (K04) for the fermentation (R02, R03, R04 and R05).

5.2.2 Fermentation

Fresh water <54> is used for the fermentation. Pressurised syn-gas <12> and air <39> are equally distributed over the fermentors. An elaborate control system is designed to ensure safe operation. The syn-gas off-gases <76> and air off-gases <77> are sent to a flare. The fermentor broth <23> is sent to the downstream processing.

5.2.3 Downstream processing

The fermentation broth is sent through a micro-filtration (S03), and the retentate <24> is sent to a mixing vessel (M02), where the t-butanol recycle is added. The t-butanol rich mixture <25> flows to the homogenisers (A02 and A03), where the cells are lysed. Centrifugation (S04) separates the product <28> from the cell debris <82>. The PHB containing stream <28> is diluted with water <87> and centrifugated (S05) again. The relatively dry product <32> is dried with the vapour stream <85> from the stripper (C01).

The debris stream <82> is led to a strip (C01). The top stream from the stripper <84> is free of debris, and is used to dry the PHB product <33>. The bottom stream <88>from the stripper (C01) is centrifuged (S07) to separate the debris <93> from the water <95>. This water stream is essentially pure and could be used for the gasifier, but this would severely complicate the process.

5.3 Utilities

The utilities for our process are mainly used for the heat exchangers and coolers. Since the gasifier is auto thermal, no heat is needed for the gasifier. The heat content of the effluent is used to its maximum extent, which led to the scenario that no additional heaters were necessary in the system. All units in the downstream except for the micro-filtration need electricity, which is the major user of energy. The units were already chosen for their minimal energy use.

5.4 Process yields

The process yields of the systems that cross the battery limit are given in Table 5-3.

Table 5-3. Process yields of the streams leaving the battery limits

IN Yield **[kg/kg-product]**		**OUT** Yield **[kg/kg-product]**	
Wood feed	11.97	PHB	1
Air feed	89.44	Off syn-gas	28.61
Water feed	8.05	Off air	68.61
Sand feed	$11.57 \cdot 10^{-3}$	Outlet debris (50%water)	0.61
T-butanol continuous	$7.72 \cdot 10^{-6}$	Broth	5.00
Nutrients	$2.78 \cdot 10^{-3}$	Exit water	6.19
		Effluent bottom ash	0.06
		Effluent fly ash	$2.78 \cdot 10^{-5}$
		Effluent tar products	$3.92 \cdot 10^{-4}$
Totals	110	**Totals**	110

The next table gives the yield based on the nominal production rate of start up chemicals.

Table 5-4: Start up chemicals. Sand and methane for the gasifier, t-butanol for the DSP.

Start-up materials	kg/kg-product
Sand start-up	$3.5 \cdot 10^{-3}$
Methane start-up	$2.66 \cdot 10^{-4}$
T-butanol start-up	$5 \cdot 10^{-3}$

From the table it can be seen that approximately 5 w-% of the wood is converted into PHB. Another remarkable component is the air. Air seems to be in large excess, but it is cheaper to transport air through the system unreacted, than to build a recycle stream. Water seems to be used inefficiently, but this is caused by the large amounts of water that are needed for fermentation. The amount of syn-gas leaving the system seems to be unreasonably large, but the process yield of the production of syn-gas is almost 30. This can be derived to growth and maintenance of the biomass.

The start-up yields are calculated as total mass needed divided by the annual production. This way the numbers can be more easily compared. The process yield for t-butanol start-up is the relative mass of t-butanol that is needed in the system in order to reach the needed concentration in the homogenisers. T-butanol continuous is the make-up stream of t-butanol that is lost in the downstream processing. It is obvious that this is stream is almost negligible.

6 Process control

A chemical process will never behave completely as it is designed, so measures must be taken to achieve product specifications and plant capacity. For example changes in feedstock composition must be compensated. The main goal of process control is to operate the plant in a safe manner. The operation of the plant is also strongly influenced by the way in which process control is carried out. Protection of the equipment is another important issue in process control.

The proposed control structure for this process is indicated in the flow sheet. The reasoning behind the control system is explained in this chapter.

6.1 Gasification section

6.1.1 Gasifier start-up

The first large unit in the system is the gasifier. The DOW Fire and Explosion Index identified the gasifier as a particularly dangerous part of the process, for this reason careful control of its operation is critical. In addition the output from the gasifier needs to be carefully controlled as it is fed to the fermentors. Failure to maintain syn-gas quality could lead to damage of the membranes, which represent a major cost to replace.

For the start-up of the gasifier a flow of methane is needed to heat the sand particles in the bed. This flow is regulated by a flow controller. A temperature sensor is installed in the gasifier to check when the temperature is high enough to commence operation. When the gasifier is in operation, the air streams <37> is controlled by a flow controller.

6.1.2 Pressure in the gasifier

The most important reactions of the gasifier are combustion of wood and gasification. The former reaction is exothermic, and uses air, whereas the latter reaction is endothermic and uses the steam. Therefore the temperature of the gasifier will be controlled by controlling the airflow <41> into the reactor. The pressure of the gasifier is controlled by the outflow of syn-gas out of the reactor and simultaneously the inflow of biomass. When the pressure in the gasifier is too low, the effluent <5> decreases, and simultaneously more biomass is added to increase pressure. One must be cautious to design the controllers accurately, in order to avoid an unstable system. Wood <4> and steam <46> flows are adjusted to maintain syn-gas quality. The syn-gas quality is based on the hydrogen concentration in the effluent.

6.1.3 Steam separation and water recycle

The flow in the water recycle <50> is determined by the flow of water out of the system through stream <52>. This stream is controlled, because it is essentially a purge stream, so it should not be too large. The water inflow <44> is a combination of a recycle and fresh feed. A vessel (V04) is added in order to control the water recycle in the system. A level controller in vessel (V04) determines the inlet flow of stream <43>.

6.1.4 Syn-gas clean-up

The filter (S02) needs periodic cleaning, because of fouling of the pores by tar. The more tar deposited on the filter, the higher the pressure drop. A pressure sensor in stream <10> therefore indicates when the filter needs to be cleaned. The effluent from the filter <10> is cooled, so a temperature controller is necessary to control the temperature for further processing. This level controller is operated in a feed-forward manner, because the membranes need to be protected. A level controller connected to stream <11> controls the operation of the flash vessel. If the quality of the effluent is too low, hydrogen from storage is added to preserve constant operation of the fermentation.

6.1.5 Mixers

There are several mixers in the system. The operation of these units is secured by level controllers. The liquid levels in the fermentation reactors are also controlled by level controllers.

6.2 Fermentation section

The yield of the fermentation can be measured by the amount of hydrogen in the gaseous effluents. If there is hydrogen in the air effluent <64>, then hydrogen is being stripped, and less syn-gas should be fed. By comparing the flow and quality of the syn-gas feed <12>, the conversion of hydrogen can be calculated. This is a measure for the conversion, which can then be connected to the PHB production per unit. If the concentration of hydrogen in the effluent is too high, less hydrogen should be fed. A similar control structure is proposed for the air streams around the fermentation.

Fermentation is an exothermic process. Therefore heat jackets are installed. Temperature controllers are needed to maintain a constant temperature in the fermentors (R02, R03, R04 and R05).

For the fermentation to run continuously at a set level, hydrogen is sometimes added as additional feed if the gasifier gives problems. Therefore a quality controller (hydrogen sensor) and a flow measurement are installed in stream <12>. If the measured amount of hydrogen is too low, a flow controller in the hydrogen stream adds more from the storage tank (V05).

6.3 Downstream processing section

6.3.1 Homogenisers

The homogenisers are essentially pumps that work at high pressures. The homogenisers can therefore control the flow through the first centrifuge (S04).

6.3.2 Centrifuges

Centrifuge (S04) effluent <28> should be controlled to maintain a minimal cake thickness in the centrifuge. The cake thickness is essential for correct operation the centrifuge, if it becomes too thin, unclarified liquid will escape in the sediment stream and the centrifuge stops functioning.

The same line of reasoning can be applied to the other centrifuges (S05 and S07). Another aspect of centrifuges is the clarity of the fluid leaving the centre of the centrifuge. The faster the rotation of the centrifuge, the better the separation. Therefore it is possible to control the quality, opacity, of the centre effluents, streams <82>, <92 and <100> by adjusting the rotational speeds of the centrifuges.

6.3.3 Cyclone

The pressure in the cyclone can be indirectly controlled. The capacity of compressor (K05) can be adjusted in order to maintain a specified pressure in stream <85>.

Stream <86> is heat exchanged to yield a liquid. If stream <87> is too warm, the coolant flow should be increased.

6.3.4 Stripper (C01)

The stripper C01 needs several controllers. The temperature is controlled by adjusting the steam flow <97>, since the steam is the major heat supplier of the stripper. The gaseous top stream is used to control the pressure in the stripper. The liquid bottom stream is cooled by a heat exchanger. A temperature controller in stream <90> controls the duty of the heat exchanger. If the temperature of stream <90> is too high, the coolant flow is adjusted accordingly. The water stream <92> from the final centrifuge (S05) is split in three streams. Stream <98> is sent to a recycle, this controlled to ensure correct solvent composition in V06. Stream <96> serves as the steam supply for the stripper (C01), this stream is varied to maintain column temperature. The water stream that leaves the system, stream <95>, serves as a wild stream.

6.3.5 Water recycle

The water recycle is a complicated control problem. To facilitate control a buffer vessel (V06) is placed after stream <102>, this vessel also serves the purpose of solvent storage during process shutdown. The vessel contains a t-butanol/water mixture with a prescribed t-butanol concentration (30%). Since the centre stream from the product centrifuge (S05) cannot be controlled, stream <98> is flow controlled to maintain the total recycle flow at a constant quality. Stream <102> is under quality control to maintain the t-butanol concentration. The t-butanol make-up serves for quality control. The t-butanol make-up is relatively small compared to the recycle stream. The addition of t-butanol make-up can generally be neglected. If too much t-butanol is added, it will dissipate in slowly over time.

7 Mass and heat balances

For the calculation of the mass and heat balance the Aspen flow sheeting program is used. The results of Aspen indicate that all the mass and heat streams are in balance. The results are copied to an Excel-file to check the mass and heat balances per unit. The results can be found in appendix 1-8.

All the mass and heat balances are in balance for every piece of equipment expect for the gasifier (R01). There is an imbalance of -1391 kW; this is probably caused by the fact that wood enters the reactor at ambient conditions and this needs to be heated. The gases entering the reactor also need to be slightly heated. This amount is about 20% of the total heat produced in the gasifier.

The overall heat and mass balances are in balance, although there is a slight difference in the ingoing and outgoing mass of the whole system. This difference is caused by round off errors. Since small numbers are sometimes used the errors made are relatively larger.

The overall mass balance consists of all incoming and outgoing streams. During the process wood is converted into syn-gas, this is fermented by bacteria to produce PHB. After the fermentation the bacteria are destroyed and the PHB will be harvested.
The incoming streams are: wood feed <1>, sand feed <34>, methane feed <35>, air feed <37>, feed nutrients <53>, feed fermentation water <54>, and feed t-butanol <78>.
The outgoing streams are: PHB product <33>, effluent bottom ash <47>, effluent fly ash <48>, effluent tar products <49>, exit water <52>, exit syn-gas <76>, exit air <77>, discharge P13 <81>, outlet debris <94>, and outlet water <95>. Table 7-1 shows the overall mass and heat balance.

Table 7-1: Overall mass and heat balance

Name:		**Total Plant**	**IN**	**Total plant**	**OUT**		**IN-OUT**
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00	0	0	0	0		
Hydrogen	2.02	0	0	0	0		
Methane	18.02	0	0	0	0		
Water	16.00	0.29	0.0160	0.417	0.0231		
Carbon monoxide	28.01	0	0	0.198	0.0071		
Carbon dioxide	44.01	0	0	0.251	0.0057		
Oxygen	31.99	0.75	0.0235	0.576	0.0180		
Nitrogen	28.01	2.47	0.0882	2.473	0.0883		
Benzene	78.11	0	0	0	0		
Phenol	94.11	0	0	0	0		
M-cresol	108.11	0	0	0	0		
Toluene	92.14	0	0	0	0		
Indene	116.16	0	0	0	0		
Fluorene	166.22	0	0	0	0		
Anthracene	178.23	0	0	0	0		
Pyrene	202.26	0	0	0	0		
Naphtalene	128.17	0	0	0	0		
Hydrogen sulphide	34.08	0	0	0	0		
Nitric oxide	30.01	0	0	0	0		
Nitrogen oxide	46.01	0	0	0	0		
Sulphur	32.07	0	0	0	0		
Chloride	70.90	0	0	0	0		
Hydrochloric acid	36.50	0	0	0	0		
Pyridine	79.10	0	0	0	0		
Ethane	30.11	0	0	0	0		
Ammonia	17.03	0	0	0	0		
Tert-butanol	74.10	$2.78 \cdot 10^{-07}$	0.0000	0	0		
Wood	1012.00	0.43	0.0004	0	0		
Ash		0	0	0.002015	0		
PHB		0	0	$3.60 \cdot 10^{-02}$	0		
Bacteria		0	0	$1.20 \cdot 10^{-02}$	0		
		0.0001			0		
Total		3.94	0.13	3.97	0.14	0.02	0.01
Enthalpy	[kW]	-7525		-7525			

8 Process and equipment design

After the tasks have been converted to unit operations the unit operations have to be designed. In this phase of the design, much has to be decided upon, such as reactor types and specific conditions. This chapters deals with the issues specific for the design.

8.1 Integration by process simulation

Microsoft Excel is used for simple calculations as well as for the economic evaluation. For the simulation of the entire process, Aspen was used. Aspen is a capable software package within a certain limited range of tasks. However for the modelling of non-standard systems, such as bioprocesses, it can be extremely hard to persuade the application to behave as desired. Aspen appeared to be particularly useful for the design of the gasification (R01) and the stripper (C01).

The simulation of the gasifier gave some difficulties, but they were solved eventually. One typical annoyance of Aspen was the separation of particles from the gas stream. A sheet was placed after the gasifier to separate off the largest particles, because they would normally remain in the gasifier. However, the gas left the sheet with the large particles, so the large particles and the gas were split in a different (fictitious) unit. Then the small particles were remixed with the gas, in order to be able to model the cyclone for removal of the small particles.

In order to design both reactors used in the fermentation Matlab was used to solve the mass balances presented in appendix 2-3. Matlab is a technical computation program, which is very useful to solve non-linear differential equations such as used to design the reactor. No major problems were encountered with this program.

A Matlab script is written to solve the mass balances over the reactor, the membranes and the bubbles. After solving the balances essential data required for the dimensioning of the reactors and design of the DSP were acquired. This section deals with the input parameters, the design procedure followed and the dimensions of the fermentors.

8.2 Equipment selection and design

8.2.1 Pretreatment

From the Aspen simulation it follows that a jaw crusher would be most suitable for the desired performance. The equipment specifications are added in the specification sheet in appendix 5-4. However, According to Coulson and Richardson vol.6 [Sinnot 2000] and Rictec [2004], a machine builder, a jaw crusher gives particles that are too big. Wood is a very tough (class 4) material and to get 5 mm particles, a hammer mill would be a better option and is therefore selected. The design of the mill is explained in appendix 3-3.

8.2.2 Gasification

Reactor entrance

After grinding, the wood particles are led to a hopper, which is the first unit of the reaction system. This hopper consists of two chambers. The first chamber operates under normal pressure, the second under elevated pressure. This is achieved by air compression. Beneath the second chamber there are two screws, a slow one and a fast one. The latter feeds the reactor by quickly shooting the wood chips into the gasifier, which is a fluidised bed, brought into motion by a stream of hot air and hot steam.

Start-up

To start up the reactor, an extra stream with methane is needed. A valve closes when the reactor reaches operational temperature and wood can be fed. From the heat capacity and total mass of sand, it is determined that approximately 1325 kg methane is needed to heat the reactor to 1000 ^oC.

Reactor

The results from the kinetics and the Aspen simulation yielded very different results. As the kinetic results did not approach those found in the literature, the Aspen thermodynamic values were used to determine the syn-gas composition. The kinetic model does not yield reliable values due to unreliable kinetic constants, predominantly for the oxidation of char. No good parameters were available for the frequency factors and the Arrhenius energies as there was no consensus between the different references or due to unclear formulae. The model could work, if these parameters were different.

The reactor is a fluidised bed which is 98 w-% filled with sand (d_p=0.5mm). The sand is needed for heat control. This fluidised bed reactor (FBR) is operated at a temperature of 1000 ^oC and elevated pressure (5 bar). Low pressure is thermodynamically favoured, high pressure results in a smaller reactor with better fluidisation velocities. Therefore this is a trade-off. Furthermore, the fermentation is operated under pressure too. This argument was the decisive factor to work with 5 bar, even if that could mean higher reactor costs. Whether this is really true or not could be calculated. However it should be noted that a standard pressure FBR would be 5 times larger ($pV = nRT$) and that retention times would be too low.

The process consists of three steps, occurring simultaneously. First there is the pyrolysis. This is the fastest step and transforms the wood to char, tar and combustible gases, the so-called pyrolysis gas. In fact, pyrolysis is best performed at a temperature of 1000K. Next there is the combustion of char and tar to CO_2 , CO and H_2O. This is the exothermic reaction providing the energy for the other steps, but this only works at higher temperatures. An advantage of the high temperature is that the thermodynamic equilibrium of syn-gas is better achieved at high temperatures. The actual gasification, which is the forming of syn-gas, is the last of the reactions. In different gasification designs, this unit is mostly operated at 1100K, because at higher temperatures sintering problems could arise. Appendix 3-2 discusses different reactors. However, in this design the actual gasification is operated in the same vessel and therefore the higher temperatures are chosen.

The fluidisation calculations can be found in appendix 3-3. The most important results are given below

Table 8-1: Fluidisation calculations

Parameter		
Residence time	3	[s]
Fluidisation velocity	1	[m/s]
Freeboard height	5	[m]
Bed height	3	[m]

The fluidisation velocity is the velocity of the gas. The velocity should be such that the sand behaves as a fluid and is therefore said to be fluidised. The residence time is the average time that a reactant spends in the reactor before leaving the system. The freeboard height serves two goals. First, it leaves space for expanding product gases. The second goal of the freeboard zone is to prevent flying sand from leaving the reactor over the top. The freeboard zone is sufficiently large to keep most of the sand within the system. The bed height is the height of the stagnant sand, without any gases. This is an important design variable.

The gas leaving the reactor is cleaned by one cyclone and a filter. Then it can be led to the fermentation as the H_2S, SO_x, NO_x and fly ash particles still left are below legislative demands or can be dealt with downstream. Below the design of the FBR is shown.

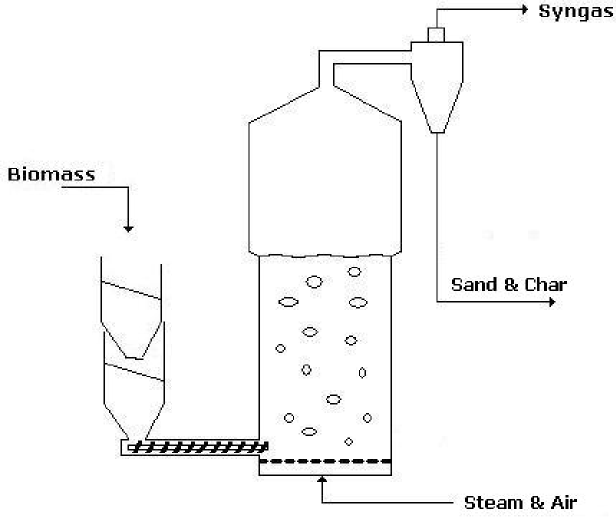


Figure 8-1: A fluidised bed reactor

The complete dimensions are given in appendix 3-3.

The whole gasification was modelled in Aspen Plus. The development of the model is explained in appendix 1-14. Here also the exit gas composition is given. The mass percentages of the main components are given in Table 8-2:

Table 8-2: Weight-based compostion of syn-gas

Comp	w-%
H_2	0.02
CO	0.20
CO_2	0.24
H_2O	0.01
N_2	0.53

Grid

As biomass doesn't contain as much ash as coal, the bottom ash can be handled using a grid at the bottom of the gasifier. Thus, large particles that cannot be fluidised can leave the gasifier. This grid is not further worked out.

Gas distributor

The gases that enter the reactor (air and steam) must be distributed evenly over the area of the FBR. Therefore a specific device has to be chosen to do this. A few demands for gas distributors are important; the distributor has to give a uniform distribution of the gas, it should be able to operate for a long time without blocking and it should be strong. Various types of distributor exist; a porous plate, a perforated plated, and a nozzle distributor. The perforated plate is the simplest design, often two perforated plates are used, which sandwich a metal screen to prevent raining of solids. This design is sufficient in this process. Table 8-3 shows the dimensions of the distributor. The calculations for the design can be found in appendix 3-3. Bubble coalescence is a potential problem in this gasifier, this potential problem could not be addressed within the available time.

Table 8-3: Gas distributor dimensions

Coefficient			Unit
Drag coefficient	C_d	0.864	[-]
Superficial orifice velocity	u_{or}	44.7	[m/s]
Number of holes	N_{or}	1780	[-]
Pitch	Pitch	0.023	[m]
Jet length	L_j	0.0016	[m]

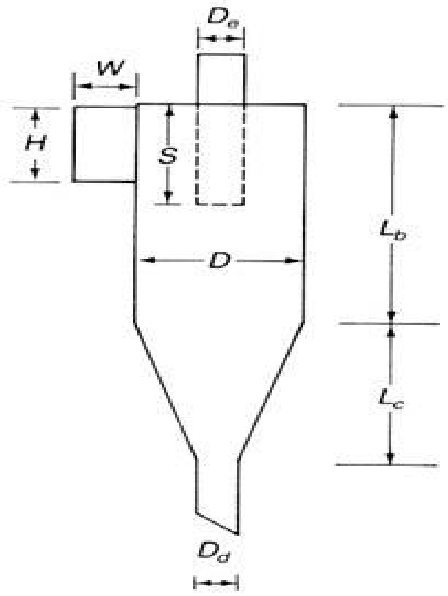
The drag coefficient is a measure of the friction in the orifice. This determines the superficial orifice velocity. The pitch signifies the horizontal distance between two holes. This number follows directly from the number of holes. The jet length is the distance that the gas can travel without mixing with sand. The parameters that define the design are further explained in appendix 3-3.

Cyclone

The gas exiting the gasifier contains small solid particles and a little aromatic vapour. These contaminants have to be removed to ensure a long membrane life in the fermentation and for environmental considerations. Therefore a cyclone is placed right after the FBR. Aspen plus calculated the cyclone data, given an efficiency of 95%, which is a realistic value (De Jong [2003], Rhodes [2000], Sinnot [2000]) and the particle distribution in the outgoing gas flow. This particle size distribution is based upon the results from the crusher in Aspen. It is assumed that particles larger than 200 μm do not come with the gas. They leave the reactor at the bottom. This assumption was necessary to use Aspen to design the cyclone because the programme cannot handle larger particles within a cyclone. This is a viable assumption, because particles larger than 50 μm could settle by gravity [Sinnot 2000].

Table 8-4: Cyclone dimensions

Parameter			
Diameter cylinder	D	1.03	[m]
Efficiency		0.90	[-]
Length of vortex		2.56	[m]
Length cylinder	L_b	1.55	[m]
Length of cone	L_c	2.59	[m]
Diameter gas outlet	d_e	0.52	[m]
Length of gas outlet	S	0.52	[m]
Width of gas inlet	W	0.21	[m]
Height of gas inlet	H	0.52	[m]
Diameter solids outlet	D_d	0.39	[m]
Number of gas turns		7	[-]
Inlet/saltation velocity ratio		1.22	[-]
Overall height		4.14	[m]



Filter

As the cyclone cannot handle the smallest particles, a ceramic filter was placed after the cyclone (De Jong [2003]). The advantage of this filter is that it can be burned clean periodically to remove condensed tar. This is necessary, as a little bit of tar has to be removed too. Slowly the filter becomes fouled and needs to be cleaned. Design criteria are given again by Aspen. The values are realistic as is discussed in appendix 3-3. It is a good idea to have a number of filters operating in swing mode, so cleaning a filter does not require the whole gasification section to shut down. This is a small additional investment.

Heat Exchangers

The water and air that enter the reactor are heated by the effluent. The effluent temperature needs to be lowered to 40ºC for the fermentation. First the effluent is cooled by the incoming air <40> in a shell and tube heat exchanger. The air is heated up until 900ºC. Then the outgoing gas is further cooled down by the incoming water <44>, again in a shell and tube heat exchanger. The steam comes out with a temperature of 850ºC. Further cooling is still needed since the gas has a temperature of about 950ºC. Another shell and tube heat exchanger is used to produce steam from the water stream <96> to the stripper. This water leaves the exchanger at 300ºC, and the effluents is cooled down to a temperature of 884ºC. After the cyclone and the filter the stream is further cooled tol 40ºC by cooling with water.

Gas-Liquid separator

The stream of syn-gas will have a temperature of 40ºC after the cooler. This means that liquid water is a big part of the stream (±1860kg/hr). This has to be separated from the syn-gas. It should be noted that the pressure is still 5 bar and that the water may be sour, as some H_2S and HCl are present among others. Thus, the separator has to withstand this. Stainless steel should be sufficient. Part of the water could be recycled, providing all the necessary water for the gasifier. Part should be purged to prevent the accumulation of inorganics. Typical retention times for the liquid are 10 minutes. If the time would be smaller, water could come with the gas stream. A preliminary design is given in appendix 3-8.

8.2.3 Fermentation

Constraint data

Assuming a loss of PHB of 5% in the downstream processing, $3.7 \cdot 10^{-2}$ kg/s of PHB has to be produced during the syn-gas fermentation to achieve the nominal PHB production rate of $3.4\ 10^{-2}$ kg/s.
According to Byrom [1987] Alcaligenes Euthrophus can store PHB up to 80 w-% of its dry weight. The optimal pH for fermentation lies around 7, so this is also used in the fermentation. The PHB storage rate is independent of the amount already stored [Suzuki 1986]. Because the residence time distribution of the chosen reactor is not a Poisson distribution, the achieved PHB content of the cells is assumed to be 75 w-%.

In biological processes the downstream processing consumes high quantities of water, chemicals and energy because of a high degree of heterogeneity and low product concentrations in the fermentation broth. In order to reduce the water streams the total cell concentration is maximised (200 kg/m^3) [Suzuki 1986] and consequently the liquid flowrate is minimised. (For more information, see appendix 8-2). Table 8-5 gives the most relevant data for both reactors.

Table 8-5: Constraint data for the design of the reactor.

		Growth Reactor	Production Reactors	
Total Cell concentration	C_{tot}	50	200^*	[kg/m^3]
Residual cell concentration	C_x	50	50	[kg/m^3]
PHB concentration	C_{PHB}	-	150^*	[kg/m^3]
Liquid flow rate	$?_{v,liq}$	0.24	0.24	[kg/s]
Reactor temperature	T_r	40	40	[°C]
Pressure at reactor top	P_{top}	5	5	[bar]
Diameter membranes	$D_{membranes}$	$1.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	[m]
Thickness membranes	$d_{membranes}$	$25 \cdot 10^{-6}$	$25 \cdot 10^{-6}$	[m]
Pressure inside membranes	$P_{membranes}$	10	10	[bar]
Height / diameter ratio	H/D_{ratio}	2.3	2	[-]
Cooling surface	$A_{cooling}$	5	5	[m^2]
Inlet cooling temperature	$T_{cooling}$	15	15	[°C]

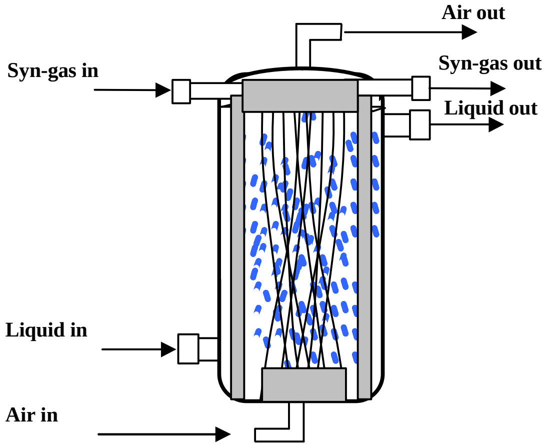
Design

The design of the reactor is performed as follows. First a required mass transfer of energy equivalents was calculated. Energy equivalents are the accumulative amounts of energy sources, in this case hydrogen and carbon monoxide. This was done by means of the information on the stoichiometry of the micro-organism (see appendix 2-1) and the required PHB production rate. Then the mass balances (differential equations) that describe the mass transfer over membranes and gas bubble into liquid (broth) were set up (see appendix 2-3). Since the reactions were mass transfer limited the micro-organisms and PHB production rate can be described by these balances.

The mass transfer in the fermentor requires a certain membrane exchange area. This exchange area is a constant that needs to be calculated as a part of the design. The membranes should fully contact the liquid and also sparging of bubbles between the membranes must be possible, thus a maximal membrane hold-up exists (membrane volume divided by the total volume) for which this is still possible. This maximum membrane hold-up is estimated be 0.5. This estimate was made by examining the membrane bioreactors used in waste-water treatment plants for the permeation of cleaned waste water. In the appendix 2-2 two figures of Zenon membrane modules were given. With the membrane hold-up and the acquired membrane volume a reactor volume is calculated. The volume not occupied by membranes is filled by the liquid and air bubbles.

It is assumed that the air bubbles will not directly contact the membranes, since mostly a liquid film layer is formed between the membranes and the air bubbles. With the available volume for the liquid, membrane and bubble phases the fermentor is designed. The fermentor will have the form of a cylinder for better mixing properties. The initial gas flowrate and the ratio of height and diameter of the fermentor are varied in order to get the required mass transfer in oxygen. The average final gas hold-up (volume of air bubbles divided by the liquid volume) should however be around 20-30 vol-%, since higher hold-ups will give too much coalescence of the bubbles. If the required mass transfer can however not be reached this requires that a lower membrane hold-up should be taken.

The design of the bubble column will give the column or reactor height. This height determines the membrane length; with this membrane length the number of membranes required is calculated. The fermentor design is shown below.



For more detailed information see appendices 2-1 to 2-5. The obtained dimensions and parameters are given in Table 8-6.

Table 8-6: Relevant dimensions of the reactors: growth reactor and 3 production reactors

		Growth Reactor	Production Reactors	
Volume reactor	V_r	8	8	[m^3]
Number of reactors	n_r	1	3	[-]
Membrane hold up	e_{mem}	0.25	0.5	
Residence time	τ	4.8	3.7	[hr]
Membrane length	L_m	3.5	3.5	[m]
Number of membranes	n	350,000	660,000	[-]
Gas hold up vs. liquid	e_{gas}	0.3	0.2	[-]
Reactor height	H_k	4	3.75	[m]
Liquid Height	H_{liq}	3.77	3.4	[-]
Flowrate syn-gas	? $_{m,syn-gas}$	0.26	0.26	[kg /s]
Flowrate air	? $_{m,air}$	0.89	0.59	[kg /s]
Flowrate cool. medium	? $_{m,cooling}$	$2.84 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	[kg /s]

8.2.4 Downstream Processing

Micro-filtration of broth

The dimensioning of a micro-filtration unit is a straight-forward process. Since micro-filtration is usually performed in cross-flow, cake production is almost eliminated. The most important parameters in micro-filtration are the amount of liquid that passes through the membrane and the type of membrane.

The calculations that were done to come to the necessary surface area are given in appendix 4-4. The necessary surface area for the filtration is 0.92 m^2.

Homogenisation of cells

This is a standard piece of equipment. The parameters are the pressure and throughput to be achieved, these were 500 bar and 0.53 kg/s respectively.

Separation of raw PHB from debris suspension

The driving force in a centrifuge is the difference in density between the solvent and the solute. This force can be enlarged by rapid rotation. This is the principle of centrifugation. The difference in density between the PHB granules and the effective density of the cell debris here is the driving force. The t-butanol dramatically decreases the effective density of the cell debris by binding to it and increasing its effective diameter, so only PHB sediments upon centrifugation.

For the performance of the centrifuge it is assumed that 99% of the PHB particles are separated from the fluid. This value follows from experimentally determined performance for PHB recovery by centrifugation [Ghatnekar 2002]

The dimensions determined for the centrifuges are given in Table 8-7. The calculations to come to these dimensions are explained in appendix 4-4.

Table 8-7: Specifications of the centrifuges

	S04	**S05**	**S07**	
Centrifuge Diameter	0.254	0.254	0.254	[m]
Rotation Frequency	3000	2250	2250	[Hz]
Disk count	4	4	0	[-]
Disk inclination	0.698	0.698	0.698	[rad]
Sigma Requirement	$1.48\cdot10^4$	$6.67.10^3$	$6.85.10^3$	[m^2]

PHB cleaning with pure solvent

The second centrifuge is slightly larger than the first centrifuge, because the outflow has been strongly diluted. The design strategy is exactly the same as in the first unit. The dimensions determined for the centrifuge (S05) are given in Table 8-7.

T-butanol recovery and debris precipitation

The stripper precipitates the cell debris from the t-butanol/water mixture, additionally the mixture is also separated to give almost pure water. After considering numerous options it was decided to use a randomly packed column. This is because a randomly packed column is relatively cheap, has a low pressure drop and is easier to clean if fouling by cell debris becomes a major problem.

The stripper is simulated using Aspen and Sulpak. The dimensions are given in Table 8-8.
The debris is removed from the bottom product by centrifugation. The specifications for this centrifuge (S07) are given in Table 8-7.

Table 8-8: Stripper (C01) dimensions

Parameter		
Column type	Random packed	
Tray Number		
- Theoretical	9	
- Actual	9	
- Feed	1	
Tray distance (HETP)	0.5	[m]
Tray material	Nutter ring #1	
Column material	SS 18/8	
Number of rings per m^3	67100	[m^{-3}]
Column diameter	0.310	[m]
Column height	5	[m]

Extruder

Once the PHB is purified it is extruded. Because PHB has quite similar properties to those of polystyrene the extruder requires similar characteristics.

A typical barrel diameter is 0.0635 meter with a L/D ratio of 24:1, this means a length of 1.52 m. To operate at the required capacity a 37.3 kW motor drive is necessary, friction produced by the barrel produces the heat necessary to melt the polymer. In the extruder the polymer has to be melted at its melt temperature and by means of a screw it is pushed forward through the extrusion hole.

To keep the extruder at the right temperature a liquid cooling system is provided.

9 Waste

The process is designed to produce minimal waste streams. However avoiding any waste output in a process is impossible. In this chapter all waste outputs will be discussed and an environmental friendly solution for disposal will be given. Since the plant is built in the Netherlands, the Dutch emission regulations are used as a reference. All dead-end streams of the process and their contents are given in Table 9-1. These streams will be discussed separately below. If the streams do not comply with environmental regulations treatment methods will be performed prior to crossing the battery limits.

Table 9-1: Dead-end streams of the process and their contents

Stream No	Stream type	Mass flowrate [kg/yr]	Content	Percentage w-%
47	Bottom Ash	57.600	Ash	100
48	Fly Ash	29	Ash	100
49	Tar	400	TAR	100
52	Condensed Water	4.780.800	H_2O CO_2 N_2 Sulphur compounds Nitrogen compounds	97 2 1 <<1 <<1
76	Off syn-gas	29.779.200	N_2 CO_2 CO H_2O H_2 CH_4 Sulphur compounds Nitrogen compounds	57 39 4 <1 <1 <1 <<1 <<1
77	Off gas air	71.193.600	N_2 O_2 H_2O H_2 CO	77 23 <1 <<1 <<1
81	Broth permeate	5.184.000	H_2O PHB Salts Organics	100 <1 <<1 <<1
94	Debris	633.600	Water Debris	50 50
95	Outlet Water	1.526.400	Water Organics	100 <1

9.1 Bottom and fly ash

The bottom and fly ash come from the gasifier. Because these ashes originate from biomass the heavy metal content is very small and the bottom ash is thus relatively clean. The bottom ash can be used in road construction and concrete production and fly ash can be processed in cement [VROM 2002]. This way the ashes are contained and have a useful application. It is assumed that no fee has to be paid for the ashes, since the ashes are useful materials in their applications. The ashes are however not sold either but disposed off without charge.

9.2 Tar

Tar is also produced in the gasifier and contained in a ceramic filter (S02). The tar is frequently burned from the filter, after which the filter can be reused again. During the burning process the tar is transferred into carbon dioxide and water. Concerning the renewable origin of the tar this will not have environmentally hazardous effects.

9.3 Off syn-gas

The off syn-gas is syn-gas from the fermentors which has not been absorbed. This syn-gas contains low amounts of carbon monoxide, which is toxic to many organisms and low amounts of hydrogen and methane, which both have high global warming potential respectively [VROM 2004]. A small flare will be installed to further oxidise these substances. Considering the energy content of methane, hydrogen and carbon monoxide little auxiliary fuel will be necessary. It could also be possible to install a catalyst with the flare to oxidize the hazardous substances in order to minimize auxiliary fuel use. If, for some reason, no syn-gas is transferred in the fermentors the flare is used to burn all the syn-gas. Other substances are below the legal exhaust limit [VROM 2004].

9.4 Off air gas

The off gas of the air used in the fermentor contains minimum amounts of contaminants and can thus be discharged without further treatment. In a situation were the bacteria in the fermentor do not consume the syn-gas, the air in the fermentor could strip parts of the syn-gas. In this situation the air needs to be flared together with the syn-gas.

9.5 Condensed water, broth permeate and outlet water

The condensed water originates from the gasifier. This water is contains minimum amounts of dissolved syn-gas and a minimum amount of dissolved inorganic sulphur and nitrogen compounds. Because of the low concentration these streams can be send to a wastewater treatment plant.

The broth micro-filtration permeate and the outlet water originate from the downstream processing. These streams contain minimum amounts of organics from the biomass. This waste can simply be processed in a wastewater treatment plant.

Concerning the total volume flowrate of the aqueous streams crossing the battery limits there is no need for a separate wastewater treatment plant, instead local treatment plants can be used. The aqueous streams are thus disposed through the sewers.

9.6 Debris

The debris stream contains the concentrated residual biomass. This biomass can simply be recycled by gasification together with the wood. Therefore this stream does not cross the battery limits. This recycle is not added in the design, because this would severely complicate the entire design.

In general in can be stated that the plant produces minimum amounts of wastes and that all wastes are disposed of responsibly and without high costs.

10 Process safety

Safety is an important factor in the design of a plant. Not only the safety of the employees is important, but also the environment and the nearby population has to be safe. In order to investigate the safety of the plant a few tools are available, like the DOW Fire and Explosion Index (DOW F&EI), Hazard and Operability Study (HAZOP), and fault tree analysis (FTA). In this case the DOW F&EI and the HAZOP are used. First the DOW F&EI is used for almost every piece of equipment on the plant. After that a HAZOP is preformed on the most dangerous piece of equipment.

10.1 DOW F&EI

A DOW Fire and Explosion Index was determined for all process units (except for pumps compressors and heat exchangers) based on the information from Lemkowitz (2003).
The major drawback of this tool is the need for quantification of qualitative variables, which is quite difficult. Therefore the numbers that follow from the evaluation are only used as guidelines for further process development and control. The results are given in appendix 1-9. Because of the high temperatures and the presence of explosive gases and dust, the gasifier posed the largest safety threat. The units directly following the gasifier also were hazardous units due to the presence of dust particles at a high temperature. Once the particles are removed from the system and the high temperatures have been eliminated, the DOW indices dropped considerably.

The fermentation and the stripper were moderately dangerous, whereas the rest of the units are not considered to be intrinsically dangerous. The fermentation and stripper need extra safety attention because of the presence of hydrogen and t-butanol, respectively. Both gases are flammable and explosive.

10.2 HAZOP

The gasifier was the unit under consideration in the limited Hazard and Operability study (HAZOP), because it followed from the DOW Fire and Explosion Index and intuition that the gasifier would be the most dangerous piece of equipment in the process. Pressure, temperature and flows were the parameters under extensive consideration. These were supposed to be the most important aspects of the gasifier. The HAZOP results are given in appendix 1-10.

It followed that burst disks were necessary above and below the gasification bed, to prevent excessive build/up of pressure in the reactor. A second action that was very common in the HAZOP was the shut-down of the gasifier. When the gasifier is shut down, it is important that production continues. Therefore the fermentation units should have connections to a hydrogen storage, in case the syn-gas flow fails. A second consequence of a shut-down of the gasifier is the flaring of possible off-gases. If the gasifier does not work, it is wise to flare the produced syn-gas, because it doesn’t have the correct composition for the fermentation. So the bacteria won’t get the right amount of hydrogen. Depending on the status of the gasifier the produced syn-gas could be mixed with pure hydrogen in order to receive a maximum yield.

A precaution that is not very obvious is the placement of one-way valves to prevent back-flow of the reactants and products of the gasifier. This could cause pressure build up in the gasifier, causing a dangerous situation.

The importance of a good fire-extinguishing system and evacuation routine became very clear during the HAZOP. In addition it is clear that the gasifier should be located in a section of the plant where flammable materials, such as t-butanol, wood and PHB are not stored in large quanties. In addition the gasifier should be located as far from major points of human activity as possible. The ratio between air and steam also seemed to have a large influence of process safety. This is reflected in the control system of the gasifier.

During the HAZOP it became clear that one-way valves can be useful in case of abrupt pressure changes. Therefore the effluent streams out of the fermentation are also equipped with one-way valves to prevent back-flow into the fermentors.

11 Economics

A Conceptual process design isn't completed without an economic evaluation. From the economic evaluation it will follow if the process is, or can be profitable and thus if it makes sense to continue with the design. The information for the estimations and equipment prices were taken from DACE [2003] and Sinnot [2000].

As this is a conceptual design, the economic part is only indicative. Because two main reasons, details have been intentionally omitted. The first reason is because no reliable data could be found and secondly because it is not possible to make a thorough evaluation within the frame of the CPD. Small buildings, such as offices and control panels, electrical networks etc. are accounted for in the so called 'Lang'-factors, calculating indirect costs, instead of working out all minor constructions in detail. Predominantly the reactors and process equipment are designed and calculated. For this up-to-date prices from DACE [2003] were used.

When in doubt, the highest price was chosen to make sure that costs would not be underestimated. For example, as transport and painting (amongst others) are not calculated separately, choosing the higher price will probably include these costs.
Furthermore, after the economical evaluation, a few extra units were added (extruder and hopper), whereas other streams (methane for start-up) appeared to be smaller and therefore cheaper. These minor errors tended to balance each other out. Moreover, it is probably possible to buy minor equipment such as conveyor belts for a lower price than indicated by DACE [2003], just by contacting several equipment builders.

Since the prices form DACE [2003] are from the third quarter of 2003, it was not necessary to take price inflation into account. When prices were taken from Sinnot [2000], a price correction of 7% per year was taken.

To calculate all prices, first data about all equipment was needed. This was taken from flow sheet, utility costs and specification sheets. These data are given in appendices 5-1 to 5-49. Next, the prices of the raw materials had to be selected. This is also worked out in appendix 7-4. The sales price for PHB is determined by the process economics and by the market prices. As will be shown later (sensitivity analyses), this factor is the most essential factor in the profitability of the plant. Besides PHB, ash and waste-water are produced. Discharge prices or charges were estimated.
Table 11-1 and Table 11-2 give the summaries of the estimated equipment and materials costs are given.

Table 11-1: Equipment costs

	prices in k€
Reactors & Columns	792
Heat exchangers	96
Compressors & Expanders	741
Mixers & Separators	406
Miscellaneous	261
Total Equipment Costs	2,298

Table 11-2: Raw material costs and product prices

Name	Unit	Amount (ton/yr)	Price (€/ton)	Total (€)
Wood	ton	12400	13	161,200
T-Butanol	ton	5	1250	6,250
Nutrients	ton	134	245	32,800
Sand	ton	12	20	240
PHB	ton	1008	10000	10,080,000
Ash	ton	56	0	0
Water	ton	6336	0.1	634

From Sinnot [1997] the Lang factors were obtained to estimate the Fixed Capital Costs (FCC). Factor values ranging from 0.4 to 2.15 are normally applied to a mixed solid-fluid plant.

Table 11-3: Calculation of FCC, using the Lang factors

Type of costs	k€, 2004
Equipment costs	2,298
Direct costs	4,942
Indirect costs	2,896
Fixed Capital Costs	10,138

The total investment costs, consisting of the fixed costs and the so-called working capital, can be calculated. The Working Capital consists of

- Start-up
- Initial Membranes (here k€ 950,- (€25·38,000m^2) (see appendix 7-9)
- Raw materials and intermediates (the larger part of the €1,789,000,- that is left)
- Finished product inventories
- Funds to cover outstanding accounts from customers

The next table gives the estimated investment costs, license costs and working capital.

Table 11-4: Total Investment Costs, Licence Costs and Working Capital in €

Fixed capital costs	10,138,451
License costs	0
Working capital	1,789,138
Total investment costs	11,927,589

The Total Investment Costs are €11,928,000. An 85% of the Total investments costs are Fixed Capital Costs and 0% for License Costs and 15% for Working Capital.

No License costs were taken, as no patents were followed and design was not delegated but done by the design team themselves.

As the fixed costs are clear now, the production costs are needed. These are given below. The utter rightmost column gives a slight explanation.

Table 11-5: Calculation of Production costs. See also appendix 7-12

		€/yr	%	
Variable costs				
1	Raw materials	200,490	3.3	*See Tab.7.3.2*
2	Miscellaneous materials	101,385	1.7	10% of maintenance
3	Utilities	1,223,804	20.1	*See Tab.7.3.3*
4	Shipping and packaging	0	0.0	Negligible
	Sub-total	1,525,679	25.0	
Fixed costs				
5	Maintenance	1,013,845	16.6	10% of fixed capital
6	Operating labour	1,125,000	18.5	3x5x75.000
7	Laboratory costs	225,000	3.7	20% of (6)
8	Supervision	225,000	3.7	20% of (6)
9	Plant overheads	562,500	9.2	50% of (6)
10	Capital charges	1,013,845	16.6	10% of capital investment
11	Insurance	101,385	1.7	1% of fixed capital
12	Local taxes	202,769	3.3	2% of fixed capital
13	Royalties	101,385	1.7	1% of fixed capital
	Sub-total	4,570,728	75.0	
	Direct production costs	**6,096,407**	100.0	
14	Sales expense			
15	General overhead	914461.045		(14+15+16) = 15% of DPC
16	Research and Development			
	Annual production cost	**7,010,868**		
	Production cost EUR/t	**6955.2262**		

Typical values as salaries and percentages were taken from the manual and Sinnot. Operating Labour costs should be regarded as follows: 3 operators per shift, working with five shifts, each costing €75,000

Capital Charge is the recovery of the investment of the project. It is often recovered as a depreciation charge, setting a given sum aside each year to write off the costs of the plant.
The charge could be a certain percentage of the Investment costs. In this example it is 10% of the Fixed Capital. It could be argued to take the depreciation as the inverse of the lifetime of the plant, but this is not necessary. More importantly, reasonable numbers are selected, in this case being mostly between the 8 and 20%. Numbers from the manual are taken to work with (plant life = 12 y, Cap. charges = 10% FCC).

Plant overheads include general management, canteen, security and medical staff and safety. Also mechanics from outside the factory are included here. R&D will not really be needed anymore, as it could be argued that the design is ready and further development would not be done by such a small plant.

Now the major Economic criteria are calculated.

Table 11-6: NCF, Gross Income, Production Costs and profit

Production costs /t	**6,955**	**11.1.1.1 /t**
Annual production costs	7,010,868	€/yr
Sales price PHB/t	10,000	€/t
Production of PHB	1,008	t/yr
Gross Income	10,080,000	€/yr
Corrected An.prod.cost	5,997,023	€/yr
Corrected APC/ton	5,949	€/t
Net Cash Flow	4,082,977	€/yr
NCF/ton	4,051	€/t
Tax	45	%
Profit	2,245,637	€/yr

Explanation for Table 11-6
Gross Income = production$\cdot$sales price
Corrected Annual production costs = Annual production costs minus effect of depreciation; read, costs without Capital charge (in contrast to the assorted tables from Grievink [2003] page 271 [Sinnot 2000])
NCF = Gross income – corrected production costs.
Profit = NCF – Tax

Two other important variables are the Rate of Return (ROR) and the Pay-Back Time (POT). The ROR is a simple index of the performance of the capital invested. It is the ratio of the (average) annual profit to the investment made. The POT is the inverse of the ROR and indicates how many years it may take to pay off the initial investment.

Table 11-7: Pay Back Time

Cumulative net cash flow at end of project	48,995,725	€
Life of project	12	Years
Original Investment	10,138,451	€
ROR	32	%
Pay Back Time	3	Years

The Cumulative NCF is taken as Life of Project (10)$\cdot$NCF(/yr).

$$ROR = \frac{\sum NCF - OI}{LoP * OI}$$

NCF will normally differ each year. At the beginning of the project the expenditure part of NCF will consist of costs as well as of investments. In this project the membranes have to be replaced after 7 years, so in this year the costs will also be larger. The basis taken is a common year, consisting only of production costs (without Capital Charge) and sales, assuming that the product can and will be sold at the quantity and price chosen, i.e. 1,000t and €10000/t.

Finally the Discounted Cash Flow Rate of Return (DCFRR), Net Future Value (NFV) and Net Present Value (NPV) at 8% interest are calculated. In the graph below, these effects can be visualised.

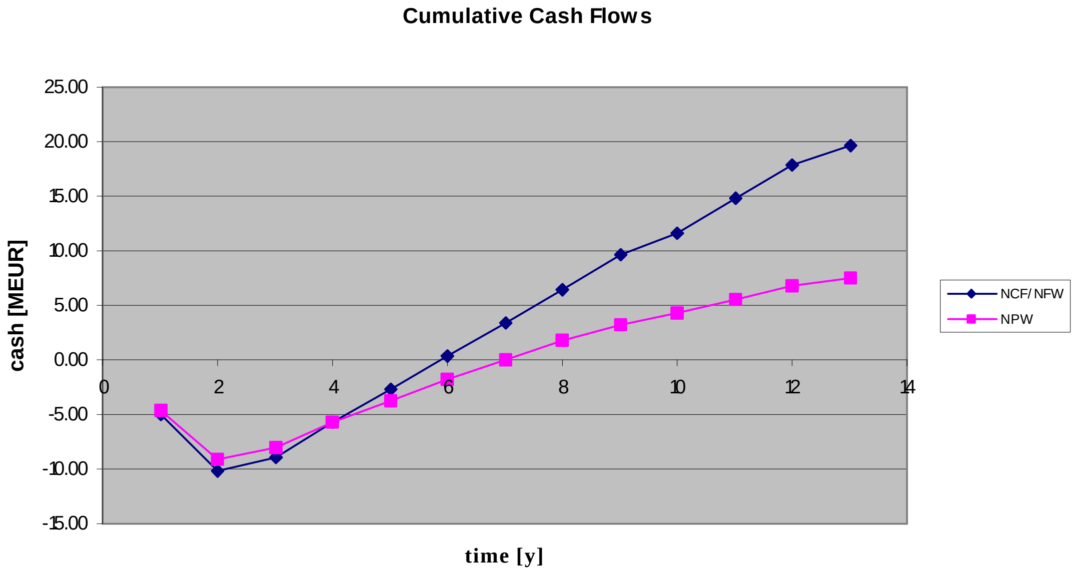


Figure 2: Discounted Cash Flow Rate of Return (DCFRR) the Net Future Value (NFV) and the Net Present Value (NPV).

The NFW is the sum of all NCFs. It indicates how much money the company can invest again or owns. As the factory starts to work in year 3, the payback time is at 6 years. This is just fine for a small plant but 4 or 5 would be better. The NPW reflects the time value of money, taking a discount rate into account (the interest rate). Finally the NCFRR gives the highest interest rate at which the project could still be feasible. For this project this is 20.5%, which certainly is not bad.

Table 11-8: Determining the NCFRR

end of year	Forecast sales, t	Forecast selling price, EUR/t TAME	Raw materials costs, EUR/t TAME	Sale income less operating costs, MEUR	Net Cash Flow, M*f*	Cumulative Cash flow, M*f* (project NFW)	Discounted cash flow at 8% or:(NPW), M*f*,	Cumulative NCF, M*f* (project NPW)	Project NPW at 30 % discount rate
1	0			0.00	-5.07	-5.07	-4.69	-4.69	-3.90
2	0			0.00	-5.07	-10.14	-4.35	-9.04	-3.00
3	1,008	10,000	198.90	3.07	1.28	-8.86	1.02	-8.02	0.58
4	1,008	10,000	198.90	3.07	3.07	-5.79	2.26	-5.77	1.07
5	1,008	10,000	198.90	3.07	3.07	-2.72	2.09	-3.68	0.83
6	1,008	10,000	198.90	3.07	3.07	0.35	1.93	-1.74	0.64
7	1,008	10,000	198.90	3.07	3.07	3.42	1.79	0.05	0.49
8	1,008	10,000	198.90	3.07	3.07	6.49	1.66	1.70	0.38
9	1,008	10,000	198.90	3.07	3.07	9.56	1.54	3.24	0.29
10	1,008	10,000	198.90	3.07	2.12	11.68	0.98	4.22	0.15
11	1,008	10,000	198.90	3.07	3.07	14.74	1.32	5.54	0.17
12	1,008	10,000	198.90	3.07	3.07	17.81	1.22	6.76	0.13
13	1,008	10,000	198.90	1.79	1.79	19.60	0.66	7.41	0.06
									-2

Project NPW at 30 % discount rate	Project NPW at 35 % discount rate	Project NPW at 20 % discount rate	Project NPW at 10 % discount rate	Project NPW at 20.5 % discount rate
-3.90	-3.75	-4.22	-4.61	-4.21
-3.00	-2.78	-3.52	-4.19	-3.49
0.58	0.52	0.74	0.96	0.73
1.07	0.92	1.48	2.10	1.46
0.83	0.68	1.23	1.91	1.21
0.64	0.51	1.03	1.73	1.00
0.49	0.38	0.86	1.57	0.83
0.38	0.28	0.71	1.43	0.69
0.29	0.21	0.59	1.30	0.57
0.15	0.11	0.34	0.82	0.33
0.17	0.11	0.41	1.08	0.39
0.13	0.08	0.34	0.98	0.33
0.06	0.04	0.17	0.52	0.16
-2	-3	0.17	5.60	0.00

After calculating all parameters, a sensitivity analysis was carried out. The purpose of this analysis is to check whether future (un)expected changes of materials or prices or wrong estimations about equipment will or will not drastically alter the balance. As can be seen from appendix 7-11, the sales price has a major and unacceptable influence on the costs. This is an unwanted situation, because market movement could render the whole factory worthless, forcing the management to follow the price or loose the competition. Both will be the end of this project.

The next largest influence on the economics is caused by the capital investments. The dependence is large and this also worrying. Fortunately the chances are smaller that this will effect the factory thoroughly, as once built, it cannot change the costs anymore.
After the capital, the people are a large cost factor, which could be expected in the Netherlands. Still, it won’t be possible to reduce the number of operators as they were already selected minimally.

What does not follow directly from these results, but is quite logically and reported in some references [Scheper 2001], building a larger plant will reduce product costs per unit. The factory should be roughly upgraded with a factor 20 to become quite competitive. The evaluation was not performed, as this would require another design of the gasifier, namely a CFBR (cycled fluidised bed reactor). This gasifier design was more complicated, but it could handle a larger feed domain. As it was not necessary for the 1000ton/yr required and too expensive for this low flow, the CFB was not designed. The FBR from this project cannot be scaled up indefinitely, as fluidisability and residence times will take their toll. Another formula indicating the upgrading profitability is:

$C = 150\ N\ (Q/s)^{0.675}$

with: plant capacity (Q) and the Capital costs (C)

N and s (the functional units and the conversion) will surely differ when considering two different designs, but still the root indicates that a lager reactor will lower costs per unit product.

11.2 Selling price

BP 2004 sells PHB for $12/kg. This price would be feasible for this plant too. This is approximately €10/kg. Therefore the predicted sales price is not unrealistic.

12 Creativity and group process tools

Creativity and group process tool play an important role in the design process. Creativity should therefore be facilitated and encouraged. Several tools were used in the conceptual process in order to improve creativity. The implemented creativity methods are the described and discussed in this chapter.

12.1 Piquar

Piquar stands for plant improvement by quality review. For this tool 5 quality factors to which the process should apply are chosen in a democratic way. These quality factors are then used to assess the process. In this design the major process choices are evaluated by subjecting them to the quality factors (Table 12-1). This is done by giving each process choice or option a score ranging from 1 till 5 (Table 12-1) for a quality factor, which stated to what extent this option complied with that factor. Each quality factor in its turn has been giving a weighting factor for its importance. This gave a clear indication to what process option should be taken. It should however be noticed that the Piquar was an important guideline in making process choices, since common sense often stated that other reasons for process choices should be considered.

Table 12-1: Quality factor chosen for the Piquar tool and their weighting factors

Quality factor	Weighting factor
Sustainability	5
Plant makes money	4
Energy, space and water efficiency	3
Efficient use of raw materials	2
Flexibility	1
Innovation	1

At first, the former 5 factors were chosen. During the project it became clear that innovation played an important role in decision-making. Thus innovation was also added to the Piquar.

Piquar has been explicitly used twice. The feedstock choice was the first use. In this case there was not a lot of discussion and everybody agreed on the outcome. The second use was the choice between the different process options for PHB production. Though Piquar already indicated what was going to be the final result, there was still a lot of discussion. These were all worked out, also because of Piquar indication for a design direction. For the choice of fermentation we did a Piquar-like assessment of reactor configuration.

12.2 Twiquar

Twiquar is a recently developed tool. It stands for Team-Work Improvement by QUAlity Review. This tool is used to improve teamwork and works essentially the same as Piquar. As in Piquar 5 quality factors are chosen to which the group should apply are chosen in a democratic way (Table 12-2). On a weekly basis the each individual team member gave a score ranging from 1 till 5 for to what extent the group work complied for each quality factor. In this way clear indication of satisfaction or dissatisfaction of each group member on a certain subject (the quality factor) became clear. The contentment on the factors is subsequently thoroughly discussed and improvements are suggested and implement. In order to get a general satisfactory for each week, weighting factors were given to each quality factor (Table 12-2).

Table 12-2: Quality factor chosen for the Twiquar tool and their weighting factors

Quality factor	Weighting factor
Feedback on contribution	5
Information sharing	4
Open discussion	3
Commitment to group	2
Members listening to each other	1

The Twiquar tool was a very useful tool for this design team. Cooperation was improved throughout the project by means of Piquar and several arguments were solved during Piquar evaluation. In Figure 12-1 the total score on the Twiquar quality factors for each week can be seen.

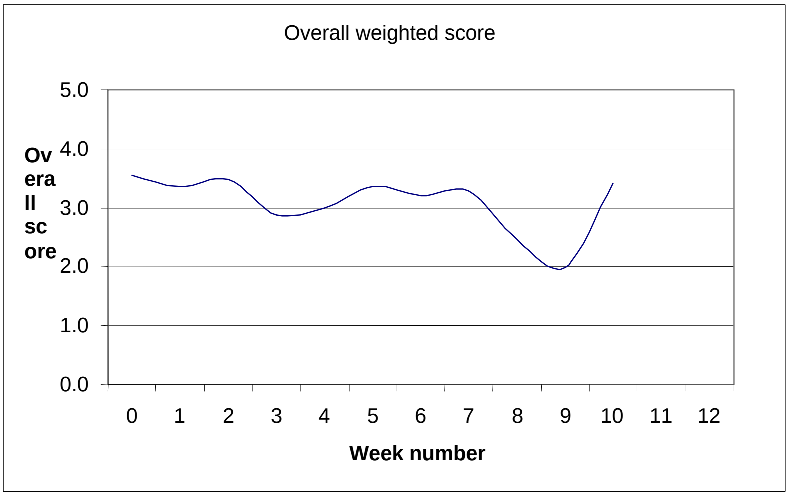


Figure 12-1: Overall weighted score of the Twiquar throughout the project

As can be seen from Figure 12-1 the group had several weeks of dissatisfaction. The thorough evaluations solved the problems almost immediately in the week following, as can be seen in Figure 12-1. Because of personal differences, which could not be solved, the Twiquar never reached high scores. This is however unavoidable and thus was generally accepted by the group.

12.3 Visiting experts

Throughout the design many problems were encountered. For several of these problems literature doesn't give a clear or consistent answer. Furthermore if one doesn't have a clear idea of what the bottleneck in a problem is or where to start looking for a solution, problem solving becomes a time consuming process with little results. To encounter these kinds of problems experts were visited. The information gathered varied from general information introducing one to a subject till highly specified information to solve problems already defined. Below the visited experts are given together with the reason of visit. Appendices 8-1 to 8-7 give detailed reviews of the visits.

Prof. F. Kapteijn: The main reason of visit was to find out what processes are available to convert syn-gas to a liquid substrate.

prof. J.J. Heijnen: The main reason of visit was to exploit the possibilities of direct synthesis gas fermentation for PHB production.

prof. M.C.M. van Loosdrecht: The main reason of this visit was to orientate ourselves in the various process and feedstock options for PHB production

dr. R.G.J.M. van der Lans: This expert was visited twice. The reason for the first visit was to get advice on how to solve the mass transfer problems in the reactor. The second visit had as a main reason to verify certain assumptions made in the downstream processing

ir. W. de Jong: The main reason of visit was to solve the problems encountered in designing the gasifier

prof. J.A. Moulijn: The main reason of visit was to check certain assumptions about the thermodynamic model of the gasifier.

12.4 DDM

The DDM stand for Delft Design Matrix. This is a tool that provides a structure in the design of a chemical process. The structure has 7 design spaces. Each design space is divided into several tasks.

The DDM was followed until design space 3. Per design space syntheses were performed, either by group discussion or by brainstorming sessions. Because of the short timescale of the project and the need to produce a report of significant proportions it was decided after the BOD meeting to focus more on production of documents which fitted the final report structure than to proceed with the DDM.

12.4.1 Planning

The advanced activity assistant (AAA) was recommended by the project supervisors to improve planning efficiency. This tool was however to complex to use, thus the design team decided to use own tools of planning.

At the beginning of the project, the minutes were used as a planning tool. Each week several goals were defined and reworked into a planning schedule. Specific task were defined during the group meetings, which took place approximately 3 times a week. In this phase of the project most of the tasks defined were derived from the DDM. The Basis of Design report however showed that the main aim of the group should be the development of the final report. Therefore an AAA-like Excel sheet was developed by the team in which the progress of the report was monitored. The motivation for developing a new spreadsheet was that this took less time than trying to understand how the AAA worked. The Excel-sheet is added in appendix 1-18. The report appendices formed the basis for the final report and were clear deliverables, which stimulated subgroup progress in critical areas. A general overview of the planning is given in Table 12-3.

Table 12-3: Planning for the CPD

Week	Start date	Tasks
1	03-05-2004	Orientation, understanding problems, understand creativity tools, prepare KO meeting (complete design space 1)
2	10-05-2004	KO meeting, Chose inputs and outputs, thorough literature study (complete design space 2)
3	17-05-2004	Complete cycle description, carry out BOD meeting and thorough literature study
4	24-05-2004	Restructuring of the planning, frequent brainstorm session, synthesis of process alternatives, finalizing mass balances, start factory design and thorough literature study (complete design space 3)
5	31-05-2004	
6	07-06-2004	Continuation of factory design, synthesis of process alternatives, reporting of appendices and thorough literature study
7	14-06-2004	
8	21-06-2004	Finalizing design, report appendices. Heat integration, structuring final report
9	28-06-2004	
10	05-07-2004	Structuring final report, finalize appendices, start of main report
11	12-07-2004	Reporting, start economy, life cycle description and waste management
12	19-07-2004	Reporting, HAZOP, process control, life cycle and finalize economy
(13)	26-07-2004	Draw conclusions, provide recommendations, finalize report

12.4.2 Group discussions

Possible choices in the process and process options were thoroughly discussed. In this way everybody gives his opinion on the different options, but moreover all essential knowledge of the individuals is spread among the group. By sharing ideas and knowledge new ideas are created which might be useful.

12.4.3 Brainstorm Sessions

This tool was used on the different design cycle stages to generate different process option to be used. Ideas were written down and afterwards the best ideas were chosen and worked out. A good example was the generation of possible feedstock materials of which the best options are worked out in the report.

13 Conclusions and Recommendations

This chapter serves to summarise the main findings of this report, based on the findings recommendations are presented for further action within the various areas touched upon. For the sake of clarity it is divided in to the following subsections: feedstock, gasification, fermentation, downstream processing, PHB and the overall process.

13.1 Feedstock

Waste wood appears to currently be in plentiful supply in the Netherlands. Utilisation of the feedstock chosen did not appear to present any special problems. Biomass is a renewable resource which is widely available. Application of poorly utilised waste streams closes material cycles. The use of waste wood for PHB synthesis differentiates this process from others for biopolymer production because it is not a feedstock which can be used to produce food products, which is a potentially sensitive issue. Waste wood is also not generally a result of subsidised agriculture so the supply is likely to remain relatively constant in the future. The cost of waste wood is extremely low compared to normal feedstocks for fermentative processes.

Drawbacks of using waste wood as a feedstock is that its composition is variable. It is produced in a dispersed manner with periodic fluctuations in supply. This makes quality control harder because numerous suppliers are likely to be needed. Transport of biomass is expensive in both economic and energetic terms. This limits the area within which feedstock can be purchased to within 50 kilometres of the plant.

Recommendation 1: Within the Dutch setting importation of biomass from other locations, such as the Baltic states, may be economically and energetically meaningful. This would require further investigation.

13.2 Gasification

The use of a gasifier to convert biomass in to syn-gas is a concept of wider utility than only this process. The use of a gasifier makes processing of virtually any carbonaceous feedstock feasible, although the actual gasifier design will determine the extent of this flexibility. Syn-gas can be used in turn as a feedstock for a long list of processes and is a common product of other processes, this makes the concept presented in this design easier to integrate in to existing plants. In addition gasification produced minimal waste streams and provided much of the energy required for the process.

Gasification does introduce problems. The unit is dangerous and its product, syn-gas, is toxic, flammable and explosive. Modelling gasification is a complicated process, although there is no guarantee that hydrolysis would have been any simpler.

Recommendation 2: Development of processes utilising gasification of biomass are currently hindered by the lack of a reliable and simple tool which accurately predicts performance. Development of such a tool would accelerate the synthesis of processes utilising biomass.

Recommendation 3: Currently the thermal energy produced by the gasifier appears to be under utilised. Better use of this energy could reduce the energy input of the process, reducing the product price.

13.3 Fermentation

The fermentation concept presented in this report has a number of strengths. The use of syn-gas reduces the risk of infections because this substrate is only useable by a limited number of micro-organisms. The substrate is very cheap compared with others typically used for fermentation. Syn-gas is a common product in petrochemical plant. Bacteria have a high tolerance towards impurities, such as SOx and can tolerate fluctuations in syn-gas composition well. The use of membranes reduced the risk of explosions significantly.

Unfortunately the membranes were a major expense in the design. In spite of their use the system remains fundamentally unsafe, with the risk of an explosion always existent. Although most substrate was used some was still wasted, in contrast to a normal fermentative process where substrate usage is virtually 100%. The final drawback was that the concept chosen was not a proven one, as far as could be determined nobody has ever tried performing a syn-gas fermentation using a membrane reactor.

Recommendation 4: The cost of membranes was a major factor in the product price. Other options for syn-gas fermentation hardware are worth investigating to try and reduce this cost.

13.4 Downstream processing

The downstream sub-process met the expectations set for it. Minimal waste was produced and there is no reason why the waste formed might not be disposed of within the process. It appears to offer a cheap way to recover PHB, with a minimal consumption of raw materials.

Unfortunately the whole concept rests of assumptions which have been extrapolated from other areas of bioseparation technology. Despite of bioseparation experts approving the reasoning applied, the truth remains that until experiments have been carried out the feasibility is not certain. Additionally the PHB produced is only 95% pure. This will certainly be acceptable for the application suggested, but will limit the applicability of the product in other areas. In comparison with other downstream processes this one is relatively complicated and start-up may well require relatively sophisticated process control.

Recommendation 5: The use of a t-butanol/water solvent can result in a potentially significant improvement in downstream bioprocessing. It is simple and worthwhile to investigate whether this is the case.

13.5 PHB

PHB possesses many properties which make it potentially a product of great interest. Its most obvious strength is its ability to biodegrade. This makes it possible to dispose of it with other compostable waste, which potentially eliminates the need for a separate collection system. Additionally PHB is not toxic or ecotoxic, it is an extremely benign substance. PHB can be blended with a variety of other biopolymers to produce plastic with a wide range of properties. Recovery of PHB is relatively simple because bacteria store it as high-density granules of relatively high purity.

More interestingly it can also be depolymerised relatively easily to yield a chirally pure compound. This chiral compound could be a starting point for a large number pharmaceutical processes based on conventional organic chemistry, which would yield chirally pure compounds.

In its pure form PHB is not a particularly useful polymer, due to excessive brittleness. Compared to a regular polymer, such as polyethylene, it is prohibitively expensive, costing nearly 20 times more. Although biodegradability can be a strength in certain applications it also limits the polymer from applications where biodegradation is unwanted.

Recommendation 6: The monomer of PHB can be easily formed from PHB. This could be a useful start point for synthesis of chirally active compounds such a pharmaceuticals. For this reason hydroxybutyrate may have potential as a key chemical for sustainable pharmaceuticals production. This is worth further investigation by specialists in organic synthesis.

Recommendation 7: Public awareness of the positive aspects of PHB is minimal. Increasing awareness is a first step to generating solid demand.

Recommendation 8: PHB can serve as a feedstock for the production of chiral compounds. This is potentially a far better application for the product that as a polymer and deserves the attention organic chemists.

13.6 The complete process

The process gained a good overall score in the final piquar evaluation. It scored particularly well on the topics of flexibility, sustainability and innovation with scores of 4.4, 4.0 and 5.0 (on a scale of 0 to 5) respectively. The concept presented here moves the sustainable production of PHB forward significantly. Major improvements are the use of a waste stream as feedstock, minimal consumption of auxiliary materials and relatively little waste production.

Scaleup of the process is certainly possible and extremely desirable. Calculations indicate that scale-up by a factor of 10 would be possible without exceeding the limits of local biomass supply. Operation on such a scale would make allothermal operation of the gasifier possible, allowing either gasification using pure steam or of oxygen. This would yield high purity syn-gas with no diluents, such as nitrogen, which in this concept constitutes 50% of the syn-gas stream. This in turn would significantly improve membrane performance, more than halving the membrane area required and fermentor volumes. It would also improve the utilisation of syn-gas. Scale-up would have a major positive impact on final product price.

The first two sub-processes, gasification followed by syn-gas fermentation, represent an interesting combination for continuous fermentation of bulk biochemicals. There is no doubt that other products could be produced using the same technology. This concept fits well in the existing petrochemical infrastructure and is flexible in both feedstock and output.

The concept presented in this report suffers from a number of deficiencies. Numerous uncertainties have been identified and they sum to produce a process which is highly conceptual in nature. These uncertainties were often dealt with by making worst case assumptions, for instance it was assumed that fermentation nutrients could not be recycled and water streams were often not recycled because the impact waste accumulation was difficult to predict. The process was also not perfectly integrated for energy consumption, this is mainly because of its size and complexity.

Ultimately the use of syn-gas results in a continually present risk. For a petrochemical process this level of risk is unlikely to be greater than is customary, however for a biotechnological process it is a significantly higher than the norm.

Recommendation 9: Water and nutrient streams can probably be recycled internally to a greater extent. However the impact this will have on bacteria performance needs to be quantified before this can happen.

Recommendation 10: This concept can be taken and scaled up for a production ten times larger. This is worth investigating but requires a complete reappraisal of each sub-process.

Recommendation 11: It is worth considering the use of other carbonaceous feedstocks and also the production of other products using a similar process.

List of Symbols

General

T	Temperature	^oC
P	Pressure	bar
R	Universal gas constant	$J\cdot mol^{-1}\cdot K^{-1}$
v-%	Volume percentage	-
w-%	Weight percentage	-

Chapter 4

r_i	Reaction rate of reaction i	s^{-1}
k_0	Reaction rate at standard conditions	s^{-1}
$E_{A,I}$	Activation energy for reaction i	$J\cdot mol^{-1}$
C_i	Concentration of substance i	$Mol\cdot m^{-3}$
K_i	Reaction constant of reaction i	s^{-1}
S	Specific surface	m^{-1}
e_c	Bed Porosity	-
k_{eq}	Equilibrium constant	-
$k_{H,inv}^{cc}$	Dimensionless Henry constant	-
P_m	Membrane permeability	$mol\cdot s^{-1}\cdot m^{-1}\cdot Pa^{-1}$
C_p	Heat capacity	$J\cdot mol^{-1}\cdot K^{-1}$
$TR_{H2/CO}$	Molar transfer ration of hydrogen and carbon monoxide	-
Δ_{liquid}	Liquid diffusion constant	$m^2\cdot s^{-1}$

Chapter 5

D_p	Particle diameter	m

Chapter 8

d_p	Particle diameter	m
C_d	Drag coefficient	-
u_{or}	Superficial orifice velocity	$m\cdot s^{-1}$
N_{or}	Number of holes	-
L_j	Jet length	m
D	Diameter	m
L_b	Length cylinder	m
L_c	Length of cone	m
d_e	Diameter gas outlet	m
S	Length of gas outlet	m
W	Width of gas inlet	m
H	Height of gas inlet	m
D_d	Diameter solids outlet	m
C_{tot}	Total cell concentration	$kg\cdot m^{-3}$
C_x	Residual cell concentration	$kg\cdot m^{-3}$
C_{PHB}	PHB concentration	$kg\cdot m^{-3}$
$?_{v,liq}$	Liquid flow rate	$m^{-3}\cdot s^{-1}$

T_r	Reactor temperature	^{o}C
P_{top}	Pressure at reactor top	bar
$D_{membranes}$	Diameter membranes	m
$d_{membranes}$	Thickness membranes	m
$P_{membranes}$	Pressure inside membranes	bar
H/D ratio	Height / diameter ratio	-
$A_{cooling}$	Cooling surface	m^2
$T_{cooling}$	Inlet cooling temperature	^{o}C
V_r	Volume reactor	m^3
n_r	Number of reactors	-
e_{mem}	Membrane hold up	-
τ	Residence time	s
L_m	Membrane length	m
n	Number of membranes	-
e_{gas}	Gas hold up vs. liquid	-
H_k	Reactor height	m
H_{liq}	Liquid Height	m
$?_{m,syn\text{-}gas}$	Flowrate syn-gas	$m^{3}\cdot s^{-1}$
$?_{m,air}$	Flowrate air	$m^{3}\cdot s^{-1}$
$?_{m,cooling}$	Flowrate cooling medium	$m^{3}\cdot s^{-1}$

List of Abbreviations

syn-gas	Synthesis gas
PBS	PolyButylene Succinate
PCL	PolyCaproLactone
PLA	PolyLactic Acid
PHA	PolyHydroxyAlkanoates
PHV	PolyHydroxyValerate
PHH	PolyHydroxyHexanoate
DBW	Domestic Biodegradable Waste
SDS	Sodium Dodecyl Sulphate
BOD	Basis Of Design
PHB	Poly-3-β-HydroxyButyrate
t-butanol	tert-butanol
DSP	DownStream Processing
NRTL	Non-Random Theory of Liquids
Inh.	Inhabitants
DCFRR	Discount Cash Flow Rate Of Return
$–[C_4H_6O_2]-$	Molecular formula representing a monomer unit build in the PHB or the dehydrolysed PHB monomer
C-mole	Molar mass based on one carbon in the molecular formula
$<CH_2O>$	Molecular formula of microbial biomass
TXY	Temperature liquid/ vapour composition
FBR	Fluidised Bed Reactor
CBR	Circulating Bed Reactor
CFB	Cycled Fluidised Bed
LHV	Lower Heating Value
HHV	Higher Heating Value
NPCM	Non PHB Cell Material
PFS	Process Flow Scheme
COMP	Component
HETP	Height equivalent theoretical plate
DOW F&EI	Dow Fire and Explosion Index
HAZOP	Hazard And OPerability Study
DACE	Dutch Association of Cost Engineers
FCC	Fixed Capital Costs
WC	Working Capital
LC	License Cost

TIC	Total Investment Costs
CC	Capital Charge
R&D	Research and Development
NCF	Net Cash Flow
APC	Annual Production Cost
ROR	Rate Of Return
DCFROR	Discount Cash Flow Rate Of Return
POT	PayOut Time
PBT	PayBack Time
OI	Original Investment
LoP	Life of Project
NPV	Net Present Value
NFV	Net Future Value
NPW	Net Present Worth
NFW	Net Future Worth
Q	Plant capacity
C	Capital costs
N	Functional unit
S	Conversion
TWIQUAR	Team-Work Improvement by QUAlity
PIQUAR	Plant Improvement by QUAity Review
DDM	Delft Design Matrix
AAA	Advanced activity Assistant

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Appendix 1:

General Appendices

Appendix 1-1: Feedstock choice

The feed stocks under consideration are willow, sugar beet, glucose and domestic biodegradable waste (DBW). They will be compared on several criteria, in order to facilitate decision-making.

Land use

Willows and sugar beet have a well-defined level of land use. Glucose can be derived from a very large number of sources so the level of land use is harder to quantify. Land use for DBW is not relevant as it is a waste stream.

Willow yields are approximately 14 dry tons per annum [Spitzley 2003].
Sugar beet is currently produced on 105 000 [Suikerinfo 2004] hectares per annum in the Netherlands with a typical yield of 15 dry tonnes per hectare (assuming a moisture content of 75%) [Tellus missie 2004].

Storage

Willow can be harvested once a year so it will need to be stored prior to processing. This is not problematic as the wood needs to be allowed to dry. The safest assumption is that the willow will need to be stored within the processing plant, although this assumption should be tested if the feedstock is chosen.

Sugar beet will require more specialised storage facilities as the high sugar levels encourage decay. Typically, intensive processing of sugar beet occurs during the few months after the harvest begins [Chemicals cost guide 2002]. This definitely places a limit on the operational freedom of the plant.

Glucose can be bought on the open market all year round and will require only small amounts of local storage.

DBW is available as an approximately constant supply although composition will probably vary slightly during the year as garden refuse production peaks during the summer and drops to almost nothing in the winter, this might be compensated by blending with waste streams from greenhouses (greenhouse production peaks during the winter).

Availability

All quantities are given on the basis of wet mass.
Sugar beet is currently produced on 105 000 [Suiker info 2004] hectares per annum in the Netherlands with a typical yield of 60 tonnes per hectare [Tellus missie 2004], giving a total annual harvest of 6300000 tons per annum.
DBW production is 1.4 megatons per annum.

Composition

The concentration of fermentable species in the various feed stocks is a very important variable, because the balance will result in waste.

Table 1. Composition of various feed stocks [Brown]

	Water	Cellulose	Hemicellulose	Lignin	Sugars	Rest
Willow	0.6	0.2	0.09	0.09	0	0.02
Sugar beet	0.77	0.02	0.02	0.02	0.17	0
Glucose	0	0	0	0	1	0

Prices

The cheaper the feedstock, the better. So it is wise to compare the prices of the various feed stocks under consideration. Table 2 shows the results. The domestic waste has a negative value, because the buyer is paid to accept this feedstock.

Table 2. Prices of the feed stocks [Heller 2003; Irish Farmers' Association 2004; FAO 2003; Bioclean 2004; PDE 2003]

	Price (€/kg)
Willow biomass	0.03
Sugar	0.10 - 0.15
Sugar beet	0.053
Glucose	0.40
DBW	–0.032

Implications for process

Willow and DBW will require pre-processing, conversion and separation steps. Sugar beet may require storage facilities, seasonal production or an alternative feedstock.

Appendix 1-2: Piquar evaluation feedstocks

The resulting Piquar values for Fruit tree wood and Rest wood were 7.9 and 8.0 respectively.

Piquar quality factors and their values

Piquar assessment week: 1

Bieten	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	8	3	4	6	3	4	4.7	3.9
Plant makes money	4	8	2	5	8	3	4	5.0	6.4
Energy, space and water efficiency	3	6	4	4	6	7	3	5.0	2.4
Efficient use of raw materials	2	9	9	5	5	5	4	6.2	5.0
Flexibility	1	4	3	2	4	4	5	3.7	1.1
overall weighted score		7.5	3.7	4.3	6.3	4.1	3.9	**5.0**	

GFT	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	8	10	8	10	5	7	8.0	3.6
Plant makes money	4	4	8	7	6	7	9	6.8	3.0
Energy, space and water efficiency	3	6	9	7	6	6	8	7.0	1.6
Efficient use of raw materials	2	8	9	8	8	8	7	8.0	0.4
Flexibility	1	8	9	8	8	7	9	8.2	0.6
overall weighted score		6.5	9.1	7.5	7.7	6.3	7.9	**7.5**	

Wilg	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	8	6	5	8	7	6	6.7	1.5
Plant makes money	4	6	3	6	8	6	4	5.5	3.1
Energy, space and water efficiency	3	6	3	5	6	7	5	5.3	1.9
Efficient use of raw materials	2	4	5	6	6	9	6	6.0	2.8
Flexibility	1	6	8	8	4	8	9	7.2	3.4
overall weighted score		6.4	4.6	5.6	7.1	7.1	5.5	**6.0**	

Hout uit fruitsector en boomkwekerij	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	9	8	8	10	8	9	8.7	0.7
Plant makes money	4	8	6	7	8	6	9	7.3	1.5
Energy, space and water efficiency	3	8	8	7	8	7	8	7.7	0.3
Efficient use of raw materials	2	6	5	8	8	9	9	7.5	2.7
Flexibility	1	6	9	8	4	8	9	7.3	3.9
overall weighted score		7.9	7.1	7.5	8.4	7.4	8.8	**7.9**	

schoon resthout incl bast vers	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	9	8	8	10	8	9	8.7	0.7
Plant makes money	4	8	9	7	8	7	9	8.0	0.8
Energy, space and water efficiency	3	8	7	7	8	6	8	7.3	0.7
Efficient use of raw materials	2	6	8	8	8	8	9	7.8	1.0
Flexibility	1	6	7	8	4	7	9	6.8	3.0
overall weighted score		7.9	8.0	7.5	8.4	7.3	8.8	**8.0**	

glucose	weighting	individual score							
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**	**Group**	**variance**
Sustainability	5	6	2	2	2	1	3	2.7	3.1
Plant makes money	4	8	5	2	2	8	3	4.7	7.9
Energy, space and water efficiency	3	6	2	2	2	9	5	4.3	8.3
Efficient use of raw materials	2	10	10	2	2	2	4	5.0	15.6
Flexibility	1	4	3	2	6	1	5	3.5	3.5
overall weighted score		6.9	3.9	2.0	2.3	4.6	3.7	**3.9**	

Striking inconsistencies in marking by team members

There were several differences in the assessments and appreciations of the individual criteria for the separate feedstocks given by the team members. Of course this was partly due to having so many feedstocks in consideration. Looking at the lines with the biggest variance, it can be said that apparently not all members took the same definition for the same criterion.

Some took the criterion widely broader than it strictly says, so they will be reviewed and adjusted for next week's evaluation.

Objectives for improvement

Adjusting the definitions of the criteria so all members will interpret the same information and thoughts similarly and probably come closer in their judgements.

Conclusions

We will go further with Rest wood, fresh including bark, and from fruit trees and tree farms. In fact one could say that Wood has been chosen, but these are the cheapest sources to obtain it from.

Appendix 1-3: Sustainability

Sustainability has high priority in this design. In order to design in a sustainable way, a definition of sustainability is chosen and criteria for sustainability are developed. Important decision and alternatives in the design will be subjected to the criteria and in this way will be judged on sustainability. The results from these judgments will be used to make to most sustainable design. This does not mean that the design will be inherently sustainable, but at least the most sustainable design possible from our scope of time and resources.

Sustainability definition

It is well known that society is not prepared to live like cavemen when all fossil fuels are depleted. So we have to look for new method's to sustain our way of living in the future. This requires the development of new technologies that do not deplete or damage natural sources to such an extent that they will limit our welfare. This brings us to the concept of sustainability. This concept provides a way of living for society in which human welfare is not limited to the earth natural sources on the long term. However the definition of sustainability is not a fact. Many people, organizations or countries interpret it in their own way and give their own definitions, meanings and goals to it, though in almost all definitions one goal is the same: "to sustain human life and its welfare".

It has to be said that it is very difficult to generate a group's view on sustainability or on sustainable development from the individual views. For this and several other reasons, there is chosen for the view or definition in the international Brundtland report "our common future " from 1987. The other reasons we choose for this definition are the following.

First and foremost the Brundtland commission's view on sustainability is in many ways in accordance with the group's view on sustainability. Secondly it is the most widely accepted and most adopted view. In order to reach sustainability global cooperation is necessary and this is only possible if everybody is working towards the same goal. In the third place the definition or view of the Brundtland commission is not a given fact, but it is in many ways free for one's own interpretation.

The Brundtland report states that:

"Humanity has the ability to make development sustainable - to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs."

It then goes on to define sustainable development as follows:

"In essence, sustainable development is a process of change in which the exploitation of resources, the direction of investments, the orientation of technological development, and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations" [rapport duurzame risico's].

These definitions do not cover the whole view on sustainability of the Brundtland commission stated in "our common future", so a bit more explanation is needed. The Brundtland Report is focused primarily on the needs and interests of humans, and was concerned with securing a global equity for future generations by redistributing resources towards poorer nations to encourage their economic growth. It was the wish of the Report that all human beings should be able to achieve their basic needs. The Report also suggested that social equity, economic growth and environmental maintenance are simultaneously possible and that each nation is capable of achieving its full economic potential whilst at the same time enhancing its resource base. However, it recognised that achieving this equity and sustainable growth would require technological and social change.

Criteria

In order to get a good sustainable process, clear sustainability goals or criteria are to be formulated. These criteria will be the guidelines during the design process and will be taken into account during process choices. In order to structure the criteria formulation the concept of sustainability is divided into three parts, namely:

-Economic issues
-Environmental or ecological issues
-Social issues

These fields were first formulated by the financial and business world and is nowadays best known as formulated by the oil-company Shell: ‘people, planet and profit’ (the triple P). In essence sustainability becomes an integration of the three fields. Each field is equally important. In order to fulfill the latter the sum of the weighting factors in each field is equal.
The design group formulated the following criteria with weighting factors for sustainability in each field:

1.1.1 Environmental / ecological criteria

- The process / product should not do damage to ecological systems outside their carrying capacity. Emissions should be minimized to acceptable levels.
- The process should only use renewable and recyclable resources. The rate of consumption of raw material for the process should not exceed the rate of raw material fixation (restoration) either by Mother Nature or by artificial means
- Materials, energy and space should be efficiently used
- Biodiversity should be sustained

1.1.2 Social criteria

- The process / product should be safe
- The process / product should be acceptable to most of the actors
- The process / product should be useful and improve wealth

1.1.3 Economical criteria

- The process should be profitable
- The product or process should have a good image

Appendix 1-4: Hydrolysis of biomass

Introduction

Hydrolyis was examined as a pretreatment option for cellulosic feedstock. There are three types of hydrolysis, strong acid hydrolysis, weak acid hydrolysis and enzymatic hydrolysis. All types of hydrolysis have their advantages and disadvantages. This report explains the different processes and evaluates the advantages and the disadvantages of the different types of hydrolysis. It should be noted beforehand that hydrolysis can only be economical when a very large plant is built (10,000 tons/y).

Hydrolysis, general

Wood consists of many components. The most important components are hemicellulose, cellulose and lignin. Additionally, wood consists for a few percent of extractives (terpenes, resins and phenols) and non-extractives (e.g. ash).
The main goal of hydrolysis is to convert the hemicellulose and the cellulose into glucose. Therefore the lignin should be removed. This is quite difficult because of the intimate, entwining configuration of lignin and cellulose. Besides, the majority of the cellulose is crystalline, which complicates the deterioration to glucose. Amorphous cellulose is broken down more easily.

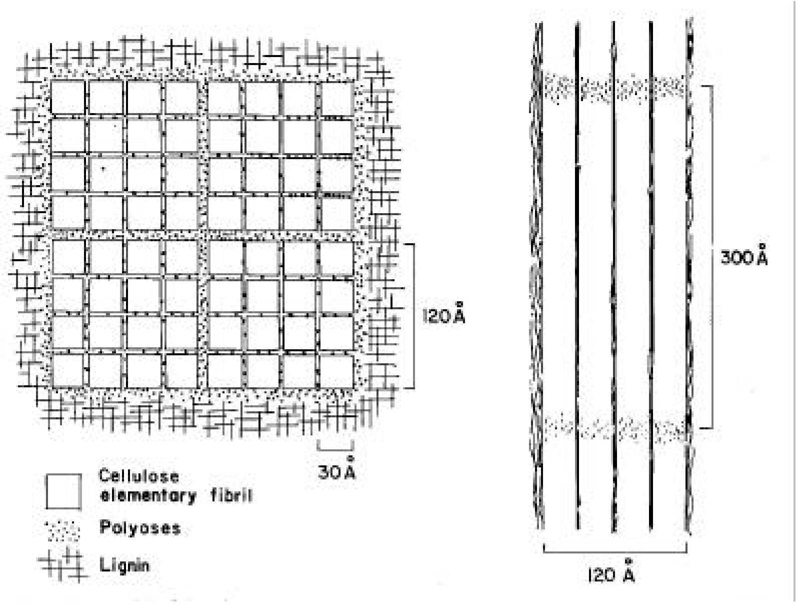


Figure 1. Model of the structural organisation of the cell wall components of wood (fan et al. 1987)

There is a difference in the lignin content of hardwood (broad leafed wood) and softwood (pine wood/coniferous wood). Figure 2 shows the composition of hardwood and softwood.

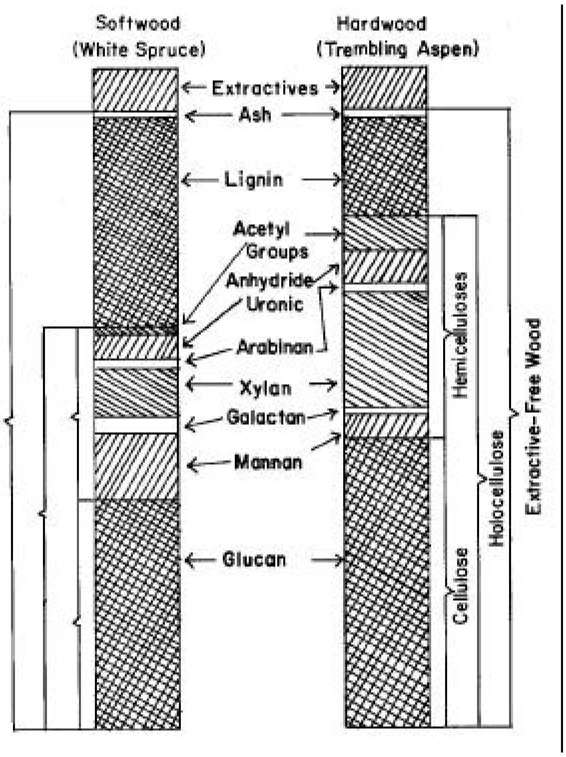


Figure 2. Comparison of the compositions of hardwood and softwood (Fan et al. 1987)

To remove the lignin an elaborate pretreatment is needed. This can be done in many ways. Table 1 gives a comprehensive list of possible and frequently used pretreatment methods.

Table 1. Methods used for pretreatment of lignocellulosics (Adapted from Fan et al. (1987))

Physical	**Chemical**	**Biological**
Ball-milling	Alkali	Fungi
Two-roll milling	Sodium hydroxide	
Hammer milling	Ammonia	
Colloid milling	Ammonium sulphate	
Vibro energy milling	Acid	
High pressure steaming	Sulphuric acid	
Extrusion	Hydrochloric acid	
Expansion	Phosphoric acid	
Pyrolysis	Gas	
High energy radiation	Chlorine dioxide	
	Nitrogen dioxide	
	Suplhur dioxide	
	Oxidising agents	
	Hydrogen peroxide	
	Ozone	
	Cellulose solvents	

  - Cadoxen
  - CMCS
- Solvent extraction of lignin
  - Ethanol-water extraction
  - Benzene-ethanol extraction
  - Ethylene glycol extraction
  - Butanol-water extraction
- Swelling agents

Mechanical pretreatment makes the cellulose more accessible to acid or enzymes by breaking lignin structures, chemical pretreatment swells the wood and cellulose and disrupts lignin.

From an economic viewpoint the caustic acid is the most attractive option for chemical pretreatment (0.12 $/kg). Sulphuric acid is a commonly used pretreatment chemical, but it is significantly more expensive (0.78 $/kg). Fitz-milling is the cheapest mechanical option (0.1 $/kg). Pressurised extrusion is the second option (0.16 $/kg). (Schell, 1978)

Process description

To make glucose from wood one can draw a main diagram as indicated in Figure 3**.**

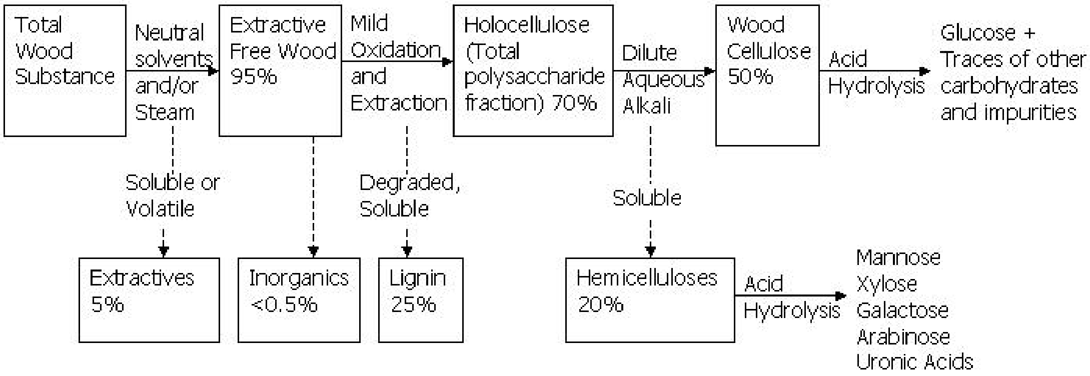


Figure 3. Classification of the major components of wood (Fan et al., 1987)

A lot of processes have been built in the last century, but they can broadly be divided in three categories, enzymatic, dilute-acid and strong acid.

Enzymatic

To make glucose from a lignocellulosic feedstock the following scheme can be regarded.

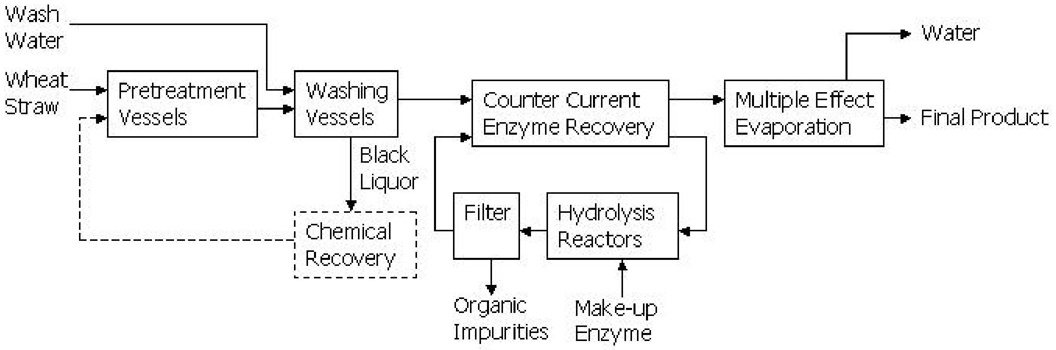


Figure 4. Schematic flow diagram for a wheat straw hydrolysis plant (Fan et al. 1987)

Wheat straw (the lignocellulosic feedstock) is pretreated with caustic soda and a slurry is formed. Part of the feed is consumed in the soda. Thereafter it is washed in a countercurrent manner and led to the reactor. Enzymes are recycled within the loop.

As can be seen, the pretreatment with the caustic solution causes a waste stream, called the black liquor. In the filter after the reactor unreacted straw is removed.

The black liquor is processed further because of the costs of the sodium, lime and waste disposal. 90% of the sodium and 97% of the lime can be recovered. The organics are burnt and provide enough heat for the evaporators and the pretreatment process. Finally $CaCO_3$ is left. This is decomposed in a furnace which will need fuel. The costs of this pretreatment recovery step are low compared to the rest of the process.

This type of plant will use batch mode reactors with a residence time of app. 8 hours. Depending on the size of the factory the cost price of the sugar will be 0.6 $/kg (big plant, 500 t/d) or more for smaller ones. The main cost factors are pretreatment, utilities and raw materials.

The kinetics of enzymes are quite complex and a lot of authors have a lot of different theories about it. It also depends on the exact composition of the cellulase depending also on the micro-organism from which it was obtained. Generally one could draw the next diagram:

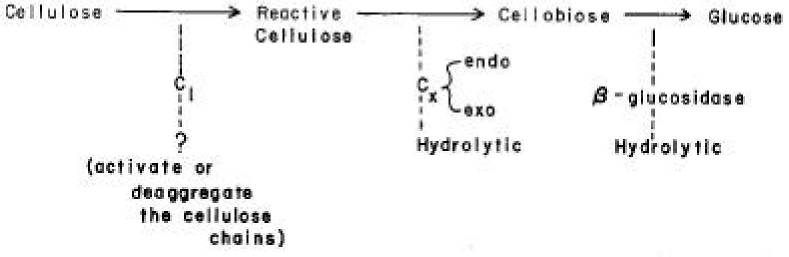


Figure 5. Degradation of cellulose (Fan et al.)

Cellulase consists of two or three types of enzymes. In this model it is proposed that the C_1 enzyme activates the crystalline cellulose and thus facilitates the hydrolytic working of the C_x. C_x can work in different ways. The endo-ß-1,4-glucanase breaks the cellulose chain somewhere in the middle and the exo-ß-1,4-glucanase will cut one small unit from the end of the chain. If this is an oligoglucoside then ß-glucosidase will transform these to glucose.

A major disadvantage of enzymatic hydrolysis is the long residence time and the costs. An advantage is the selectivity and the mild process conditions.
Until 1987 no commercial plants existed, although several studies have been done towards this goal.

Acid Hydrolysis

There are two types of acid hydrolysis, the dilute-high temperature and the concentrated-low temperature process. Further the processes can be done dealing with sulphuric acid, hydrochloric acid and phosphoric acid.

The dilute sulphuric acid process

This process is the oldest process and is usually performed in two stages. Its advantages are relatively low capital cost, easy acid separation and no need to recycle. The major disadvantage is the low yield (50-85%).
In the first stage, dilute acid (0.5-2.5%) at 130-140ºC hydrolyzes hemicellulose to pentose, in the second cellulose is converted to glucose (T=170-240ºC). Soviet plants produce 1000 tons/y of sugar, the US Madison plant (1982) produces 50t/day. A short residence time would be ideal and thus a PFR could be used, but this has only been realised on laboratory and pilot plant scale. Prices have not be found, but should be lower than enzymatic production. The major cost factors in the capital costs certainly are the acid resistant reaction vessels.
Figure 6 gives a schematic flow sheet of a dilute acid hydrolysis.

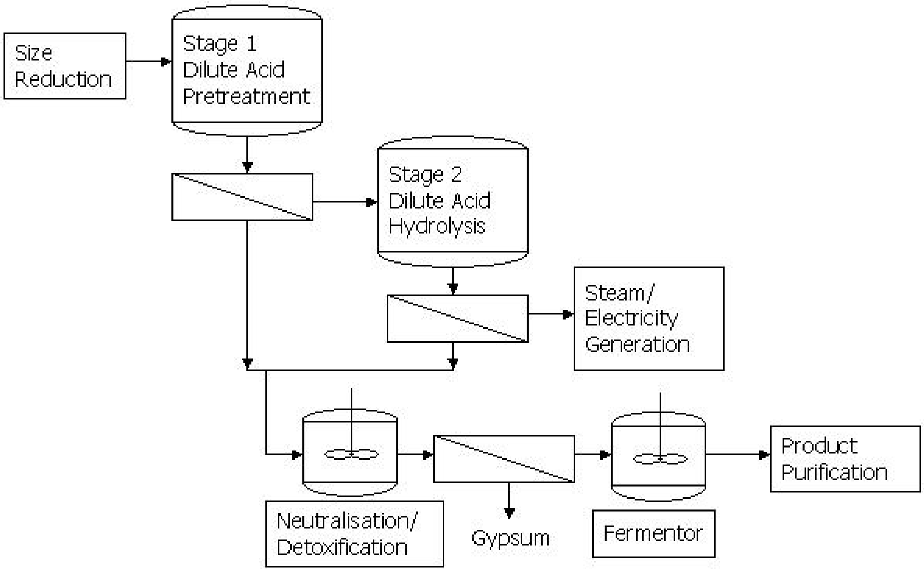


Figure 6. Process flow sheet for dilute acid hydrolysis (adapted from Department Of Energy, USA)

The concentrated acid process

Crystalline cellulose and natural hemicellulose dissolve completely in concentrated sulphuric acid (>70%, T=298K). Before 1987 only in Japan (Hokkaido) a plant was built, but recently Arkenol also built a process with a very high yield (>95%).
The process consists of three stages:

1) Prehydrolysis to hydrolyze the hemicellulose
2) Main hydrolysis of the α-cellulose

3) Post-hydrolysis to hydrolyze the oligosaccharides from step 2

Processing times for each step range from 10 minutes to two hours, depending on the exact process chosen.

A global description for these processes is given below.

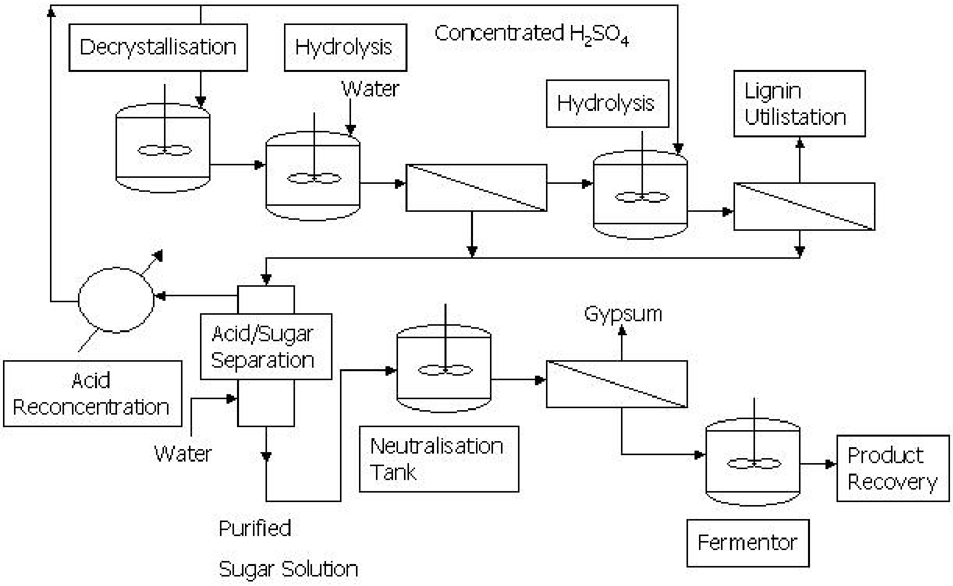


Figure 7. Process flow sheet for concentrated acid hydrolysis (adapted from Department Of Energy, USA)

The feed is mixed with recycled acid and sugars (mainly glucose) and heated to 398K with steam for two hours. The hemicellulose is converted to glucose, xylose, arabinose and acetic acid. Almost stoichiometric yields are obtained because little side reactions occur at this mild stage. Then the sugars are washed out three times. The first wash gives the product stream, the other two are recycled; the second to the first and the third to the second wash.
Then the solids are separated and water is partly removed (moisture is 55%). Acid is added and the slurry is transported to a storage vessel for two hours (low temperature prevents reaction). After thorough acid permeation the slurry is centrifuged and the liquid recycled (moisture again 55%). The solids are dried to 10% moisture (E=1100btu/lb). Now the acid is concentrated, as acid does not evaporate in contrast to water. Cellulose bonds are broken and the dry-acid impregnated solids are then mixed with water and heated to 438K with steam. Cellulose is quickly converted to glucose in a few minutes with a minimum of by-products. The slurry is separated in a flash vessel and the liquid is recycled to the prehydrolysis step. The solids are burnt for the energy of the process.
Arkenol uses sulphuric acid for the hydrolysis. The concentration of the acid is around 77%. This is then mixed with the biomass in the decrystalliser. The actual acid concentrations in the hydrolysis reactors are around 20% to 30%. The acid concentration in the second reactor is higher than in the first.

An advantage of this process is that little by-products are produced, disadvantages are energy consumption and acid recovery. The ratio of sugars produced to acid consumed is 3.5 (1.8 based on glucose solely). The ratio of water to sugars is 1:8.2 (written anno 1987, this will certainly be much less nowadays, 1:4 estimated).

Use of hydrochloric acid makes recovery easier because it is easily evaporated and thus separated, but also material costs are higher and a larger reactor volume is needed. The Germans built the “Rhiem process” after WWII.

For the concentrated acid processes, prices were not given, but the existence of commercial plants indicates that it is feasible. It should be noted that all projects speak of productions of 500 t/day.

Further processes with phosphoric acid exist.

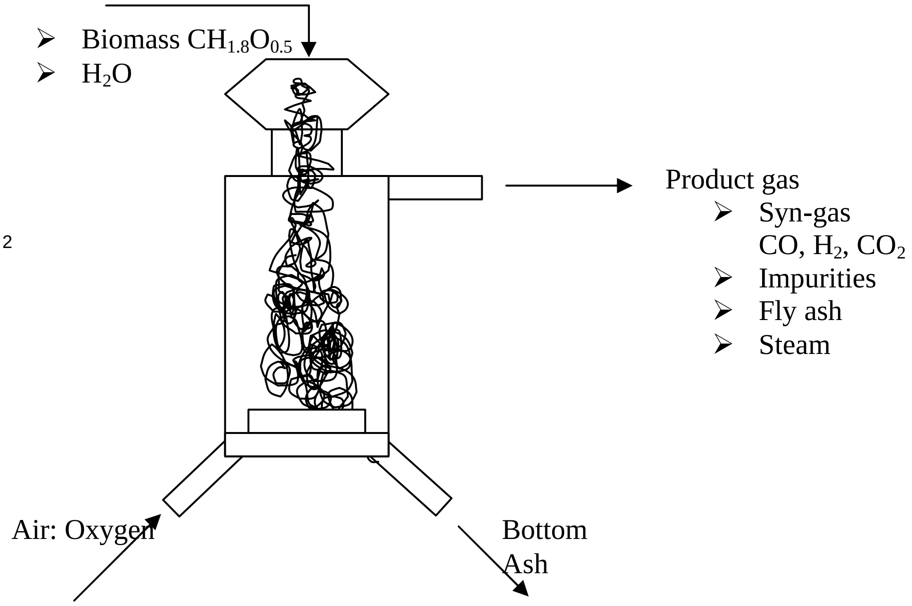
Hydrolysis with dilute acid is only suitable for fermentation, concentrated acid can produce crystalline glucose. Here, the next step will be fermentation, so both pathways are possible.

Appendix 1-5: Gasification technology

Syn-gas is a general term used to describe mixtures of hydrogen and carbon monoxide in various ratios. Syn-gas can be produced from a variety of raw materials: natural gas, coal, biomass, etc. Biomass gasification involves thermally converting biomass to simple chemical building blocks that can be transformed to fuels, products, power and hydrogen. The process is endothermic and thus requires heat. The heat may be supplied from the outside of the reactor (allothermic) or internally in the reactor by burning part of the biomass entering the gasifier (autothermic). Typical values operating conditions are: 750-1000°C and pressures ranging from 1 to 70 bars. The obtained gas is composed of mainly CO, H_2 and CO_2. High temperature gasifiers are able to convert 90% of the chemical energy of solid fuels into chemical and sensible heat of the product gas. [R.C. Brown]
The process involves:

- Feed preparation,
- The biomass gasification itself,
- Gas treatment and cleaning train

Because of impurities of the initial syn-gas is it very important to clean it before use, depending on the use. The gasification procedure also transforms the lignin into useful products. We know that lignin is the major environmental problem for the pulp industry and it would be for us when we apply hydrolysis instead of gasification. Almost every type of biomass feedstock can be transformed into syn-gas. Starting from syn-gas a very wide range of products can be produced: methanol, methane, ethanol, etc. Micro-organisms can grow on almost any organic molecule. That means that these compounds produced from syn-gas could also be utilised for growth of micro-organisms and from it produce PHB. Another option, that arose when gasification and possible feed stocks for the bacteria were investigated that is syn-gas fermentation. Bacteria that are capable to grow on H_2/CO substrates have existed since the first days of the earth.



$C + CO_2 \Leftrightarrow 2CO$
$C + H_2O \Leftrightarrow CO + H_2$
$C + 2H_2 \Leftrightarrow CH_4$
$C + ½ O_2 \Leftrightarrow CO$
$4H + O_2 \Leftrightarrow 2 H_2O$

Conversion of biomass is for the most gasifiers 90-99%. Biomass is almost completely converted to syn-gas. Besides syn-gas many other contaminants are produced. The next table gives ranges of tar, heavy metals and other contaminants produced during gasification of biomass:

Table 1: Typical values for out flow gas from gasifier. The conversion percentages are given with respect of the contents in biomass

Content in outlet from gasifier	**Units**	**min**	**max**
Carbon conversion	%	90	99
Water content	w%	5	20
Ash	wt%	0	25
Bottom ash	% of ash	60	90
Fly ash	% of ash	10	40
Tar	mg/Nm^3	300	10000
S conversion to H_2S + COS	%	100	100
N conversion to NH_3 + HCN	%	40	80
Cl, F, conversion to HCl + HF	%	80	100
Hg, Cd to gas	%	80	100
Na, K to gas	%	0	30
Metal to gas	%	0	30

Gasification of biomass has many similarities with coal gasification. There is much experience of coal gasification wastewater treatment. But some differences do exist. The first big difference is that the gasification temperature of biomass is lower than that of coal. This leads to a larger tar formation when biomass is gasified. Other difference with coal difference is the larger feedstock variety, what makes every case unique. This also holds for the wastewater composition coming from the wet gas scrubbing.

Problems of biomass gasification

Literature has shown that there are some technical aspects of biomass gasification that have to be resolved before biomass gasification is applied on a large scale.

The main problems found in gasification are:

- Feeding the fuel into the gasifier
- Tar condensation in the gas cleaning section
- Bed material agglomeration in the gasifier
- Corrosion.
- Gas cleaning equipment is not commercially proven.

What we see here is that gasification of biomass involves almost the same problems as for coal gasification, where coke is continuously formed and corrosion is also present.

Feedstock variations and properties

The main problem is that gasification needs a uniform feedstock and reliable feed preparation, storage, and handling systems. A number of feed systems exist that can function reliably using feedstock's within a narrow range of physical properties. A solution to the problem is to handle the feedstock within the plant to get uniform feed. The chemical composition of potential lignocellulosic materials can vary widely; this chemical variation can have significant effects on the economics of producing ethanol or other by-products from plant biomass.

The physical properties of the feedstock that are relevant for the gasification process are:

- LHV (lower heating value). A lower limit exists at which gasifiers can operate. When the feedstock available has a lower LHV than the lowest limit then an additional pre-treatment step is required.
- Ash and moisture content. Gasifiers have often a maximum limit for those two characteristics. Higher contents of ash and moisture require an additional pre-treatment step.
- Size, granulation, drying and sintering/slagging index. When the feedstock doesn't possess the required characteristics, which often depend of the equipment used an additional pre-treatment step is required.

The chemical properties that are relevant for the gasification are:

- The C,H,O,N content of the fuel together with the physical properties largely determine the thermal efficiency of the gasification process.
- Typical contaminants are S,CL,F alkalis metals, Hg, Cd+Tl

Gasification of biomass

The syn-gas produced

It is of utmost important that the fuel gas is described with all relevant properties. These properties are:

- LHV (lower heating value)
- Fly ash content and particle size distribution. This is originated from the inert material in the feedstock.
- Tars, the presence of this material is known as the bottleneck of the gasification process.
- Bulk gas composition (CO, CO_2, H_2 enz).
- The gas phase contaminants. They must be removed in the gas clean-up section. Relevant contaminants are: H_2S, COS, NH_3, HCN, HCl, and HF, also heavy metals are contained in the fuel gas.

The operation units

For the gasification procedure to produce syn-gas the following steps are required:

- *Preparation of feedstock*
  - Fuel milling: Rotary cutter, hammer mill, etc.
  - Fuel drying: Rotary direct, indirect, etc. Typical moisture contents range from 5 till 50 Vol% depending on the type of gasification reactor is used.
  - Fuel granulation: Roll press, Pellet mill,…
- *Gasification*
  - Reactor: Downdraft, Bubbling fluidized bed, entrained flow…
- *Gas treatment and cleaning*
  - Gas cooling/heating: Convective cooler, water quench…
  - Gas solid removal: cyclone, bag filter…
  - Tar cracking: fuel doping, catalytic cracking…
  - Wet clean-up: acid quench + wash tower….
  - Dry clean-up: Sand bed, active coal…
  - Gas upgrading: CO-shift, CO_2 removal
  - Auxiliaries: Compressor, Expander, Valve…

Syn-gas from biomass contains contaminants such as tar, particulates, alkali, ammonia, chlorine, and sulfur that have to be removed for further processing.

- For synthesis operations such as methanol and hydrogen production removal of particulates and contaminants such as hydrogen sulphide is required to prevent poisoning of downstream catalysts.

- For the case of direct fermentation of syn-gas, no strict gas clean up process is needed.

Appendix 1-6: Piquar evaluation of Hydrolysis versus Gasification

The piquar tool has been used to decide between two process options, namely gasification of the raw materials and subsequent fermentation of the formed syn-gas and hydrolysis of the raw materials and subsequent fermentation of the formed sugars. The first process scored 3.5 out of 5, whilst the latter process scored 2.9 out of five.

Piquar assessment week: 4

Hydrolysis	**weighting**			**individual score**				**Group**	**variance**
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**		
Sustainability	6	3	3	2	2	3	2	2.5	0.3
Plant makes money	5	5	4	4	4	4	3	4.0	0.4
Energy, space and water efficiency	4	4	3	1	2	2	4	2.7	1.5
Efficient use of raw materials	3	4	3	1	2	2	2	2.3	1.1
Flexibility	2	4	2	3	3	4	4	3.3	0.7
Innovation	1	2	2	2	1	1	1	1.5	0.3
overall weighted score		3.9	3.1	2.2	2.5	2.9	2.8	**2.9**	

Piquar assessment week: 4

Gasification	**weighting**			**individual score**				**Group**	**variance**
		Luc	**David**	**Martijn**	**Richard E.**	**Richard T.**	**Davinia**		
Sustainability	6	3	4	3	4	5	3	3.7	0.7
Plant makes money	5	2	4	3	2	2	3	2.7	0.7
Energy, space and water efficiency	4	3	4	4	4	3	3	3.5	0.3
Efficient use of raw materials	3	4	4	4	5	3	4	4.0	0.4
Flexibility	2	4	5	3	4	3	4	3.8	0.6
Innovation	1	4	5	5	5	5	5	4.8	0.2
overall weighted score		3.0	4.1	3.4	3.7	3.4	3.3	**3.5**	

Figure 1 Piquar Hydrolysis vs Gasification

Based on the information gathered before, everybody assigned a value to each of the criteria chosen.

Comments
In the Piquar test on hydrolysis inconsistency consists on the subject “energy, space and water efficiency” and “efficient use of raw material,” judging by the higher standard deviations. These differences are related to incomplete process knowledge, different points of view in engineering and prejudices. Furthermore, as most subjects are judged in a qualitative way instead of a quantitative way, it was a little difficult to assign a single and uniform value. Indeed, for some of the subjects it is not even possible to have hard numbers (e.g. innovation, sustainability and flexibility).

The gasification process does not have a high variance in any of the criteria. Only “sustainability” and “plants makes money” show a somewhat higher variance. The fact that sustainability shows a higher variance is due to the same reasons as for the deviations in the hydrolysis process. It is known that the hydrolysis process is not that expensive. It exists quite some time and therefore data are available. This does not count for the gasification, which is relatively new and for which no economic data are available.
This lack in “technical” or “economical” data brings about the deviations in the piquar for this subject.

Appendix 1-7: Choice of fermentation substrate

Wood can be processed to yield a wide variety of fermentation substrates. The substrate can be sugars, methane, methanol, ethanol, or syn-gas. Sugars are produced from wood by means of wood hydrolysis. Methane, methanol and ethanol can be produced by wood gasification and after that catalytic reforming. Syn-gas is always produced by gasification. Sugar and syn-gas can be produced in one step, and are therefore preferred over methane, methanol and ethanol.

The main advantages of hydrolysis over gasification are:

- The existing knowledge, hydrolysis and gasification are old and well-known processes. On the other hand fermentation of sugars is well known but syn-gas fermentation has never been applied in the industry.
- Design the hydrolysis process is easier than design the gasification step.
- Hydrolysis of wood gives as product sugars that are easily consumed by the micro-organisms.
- Less explosion and fire risks.

On the other hand gasification is preferred over hydrolysis for the following reasons:

- Gasification produces fewer wastes and is easier to operate than hydrolysis.
- Gasification doesn’t use extra chemicals in its process, just biomass, water and air, in contrast with strong or weak acids or expensive enzymes required in hydrolysis.
- Gasification of biomass requires less external energy, in contrast with hydrolysis, since the energy required is produced by combusting part of the biomass itself.
- The product of gasification (syn-gas) has many different applications.
- Possible lower investment costs, since less intermediate steps are required.
- Yield of PHB seems to be comparable.
- Innovative process, this implies high creativity and design effort
- Possibility to process any carbonaceous raw material (Waste water sludge, VGT, etc).
- Less infection chance of the fermentation step because of the exotic (toxic, due to the carbon monoxide) substrate.

Therefore syn-gas is the chosen fermentation feedstock.

HEAT & MASS BALANCE FOR STREAMS TOTAL										
IN						OUT				
Plant		EQUIPMENT			EQUIPM. IDENTIF.	EQUIPMENT			Plant	
Mass kg/s	Heat kW	Mass kg/s	Heat kW	Stream Nr.		Stream Nr.	Mass kg/s	Heat kW	Mass kg/s	Heat kW
		0.45	-5282	**<83>**	**C01**	**<84>**	0.19	-1063		
		0.07	-948	**<97>**		**<88>**	0.33	-5167		
		0.52	-6230		Total		0.52	-6230		
		1.59	-6033	**<5>**	**E01**	**<6>**	1.59	-6566		
		0.75	183	**<40>**		**<41>**	0.75	716		
		2.34	-5850		Total		2.34	-5850		
		1.59	-6566	**<6>**	**E02**	**<7>**	1.59	-7809		1243
		0.42	-6523	**<44>**		**<45>**	0.42	-5280		
		2.01	-13089		Total		2.01	-13089		
		1.59	-7809	**<7>**	**E03**	**<8>**	1.59	-8005		196
		0.07	-1144	**<96>**		**<97>**	0.07	-948		
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		0.08	-1178	**<86>**	**E04**	**<87>**	0.08	-1178		
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		0.33	-5168		Total		0.33	-5168		
				<35>	**K01**	**<36>**				
					Total					
		3.22	213	**<37>**	**K02**	**<38>**	3.22	213		
		3.22	213		Total		3.22	213		
		0.42	-4953	**<45>**	**K03**	**<46>**	0.42	-4953		
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		0.23	-3668	**<55>**						
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		0.11	-1016	**<24>**	**M02**	**<25>**	0.52	-5693		
		0.41	-4677	**<102>**						
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		0.23	-3668		Total		0.23	-3668		
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				<78>	**P05**	**<79>**				
					Total					
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		0.46	-5282		Total		0.46	-5282		
		0.27	-1748	**<29>**	**P07**	**<30>**	0.27	-1748		
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		0.41	-4674		Total		0.41	-4674		
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		1.59	-8003	**<9>**	**S02**	**<10>**	1.59	-8003		
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		0.24	-1183		Total		0.24	-1183		
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0.01	**1391**				Total					**1439**
OUT - IN :									-0.01	**48**

Project ID Number	:	**CPD3201**
Completion Date	:	31st December 1998

Unit name Aspen	**Storage**	**Crusher1**	**Gasifier**	**Splitter**	**Cyclone**	**Bag-filt**	**Cult1**	**Ferment**	**Homogeniser**	**Micro-filtration**	**Centrifuge**	**Stripper**
Gevaarlijkste component	Hydrogen	Wood	Hydrogen	Hydrogen	Hydrogen	Hydrogen	Hydrogen	Hydrogen	T-butanol	T-butanol	T-butanol	T-butanol
http://www.cheque.uq.edu.au/ugrad/theses/1998/DaveA/dow.html												
	PF	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**	**PF**
Material Factor (MF)	10	10	29	16	10	10	24	24	10	10	10	16
Base Factor	1	1	1	1	1	1	1	1	1	1	1	
A. Exothermic Chemical Reactions	0	0	0.4	0	0	0	0.3	0.3	0	0	0	0
B. Endothermic Processes	0	0	0.25	0	0	0	0	0	0	0	0	0
C. Material Handling and Transfer	0	0.5	0.65	0.5	0.5	0.5	0.25	0.25	0.4	0.25	0.5	0.25
D. Enclosed or Indoor Process Units	0.25	0.25	0.3	0.5	0.5	0.5	0.25	0.25	0.4	0.25	0.25	0.6
E. Access	0.2	0.35	0.35	0.2	0.2	0.2	0.2	0.2	0.35	0.25	0.25	0.3
F. Drainage and Spill Control	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
General Process Hazards Factor F1	0.7	1.35	2.2	1.45	1.45	1.45	1.25	1.25	1.4	1	1.25	1.4
Special Process Hazards												
Base Factor	1	1	1	1	1	1	1	1	1	1	1	1
A. Toxic Material(s)	0	0	0.7	0.7	0.7	0.7	0.2	0.2	0.5	0.5	0.5	0.5
B. Sub-Atmospheric Pressure (<500 mmHg)	0	0	0	0	0	0	0	0	0	0	0	0
C. Operation In or Near Flammable Range												
1. Tank Farms Storage Flammable Liquids	0	0	0	0	0	0	0	0	0	0	0	0
2. Process Upset or Purge Failure	0	0	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
3. Always in Flammable Range	0.8	0	0.8	0.8	0	0	0	0	0	0	0	0.8
D. Dust Explosion	0	1.5	1	1	1	1	0	0	0	0	0	0
E. Pressure												
Operating pressure	0.1	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Relief setting	0	0										
F. Low Temperature		0	0	0	0	0	0	0	0	0	0	0
G. Quantity of Flammable/Unstable Materials												
1. Liquids or Gases in Process	0.1	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
2. Liquids or Gases in Storage	0.1	0	0	0	0	0	0	0	0	0	0	0
3. Combustible Solids in Storage, Dust in Process	0	0.1	0.1	0.1	0.1	0.1	0	0	0	0	0	0
H. Corrosion and Erosion	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
I. Leakage - Joints and Packing	0.25	0.1	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.5
J. Use of Fired Equipment	0	0					0	0	0	0	0	0
K. Hot Oil Heat Exchange System	0	0	0	0	0	0	0	0	0	0	0	0
L. Rotating Equipment	0	0.5	0	0	0.5	0	0.5	0.5	0.5	0	0.5	0
Special Process Hazards Factor F2	2.85	3.7	4.85	4.85	4.55	4.05	2.95	2.95	3.25	2.75	3.25	3.8
Process Unit Hazards Factor (F1 X F2) = F3	1.995	4.995	10.67	7.0325	6.5975	5.8725	3.6875	3.6875	4.55	2.75	4.0625	5.32
Fire and Explosion Index (F3 X MF) = F&EI	19.95	49.95	309.43	112.52	65.975	58.725	88.5	88.5	45.5	27.5	40.625	85.12
Degree of Hazard	**Light**	**Light**	**Severe**	**Intermediate**	**Moderate**	**Moderate**	**Moderate**	**Moderate**	**Light**	**Light**	**Light**	**Moderate**

Appendix 1-10: HAZOP results

		Causes	**Consequences**	**Action required**
Pressure	More	• Flow reactants too high • Blockage exit of gasifier • Control system failure	• Stress on reactor • Explosive mixture • Entrainment • Too high temperature	• Install burst disk above and below the bed • Additional oxygen measurement • Link oxygen flow to the flare • Turn off the flow • Connect the fermentation to hydrogen supply from storage • Compensate air stream by steam
	Less	• Flow reactants too low • Temperature reactants too low • Burst disk failure • Pressure hopper failure • Control system failure	• Excessive tar formation • Low quality syn-gas • Insufficient fluidisation • Gas leakage • Back flow in hopper • Hot sand flying through factory	• Replace filter for cleaning • Send syn-gas directly to flare; connect the fermentation to hydrogen supply from storage • Add more steam • Replace damaged components • Install one-way valves • Install automated fire extinguishing mechanism (near gasifier)
Temperature	More	• Oxygen inflow too high • Temperature reactants too high • Control system failure • Outflow syn-gas too low	• Hot spots • Low quality syn-gas • Filter burns down • Reactor melts • Sand melts • Too hot gases melt membranes in fermentation • Insufficient fluidisation • Excessive tar formation • Filter blockage • Possible runaway • Higher pressure	• Shut down reactor; send syn-gas directly to flare; connect the fermentation to hydrogen supply from storage • Add more steam for better fluidisation • Evacuate the factory • Adjust water/air ratio • Extinguish fire • Cool the reactants • Change to new filter • Lower the inflow of reactants

PURE COMPONENT PROPERTIES

Component Name		Technological Data								Health &Safety data								
Design	Systematic	Formula	Mol. Weight g/mol	Phase	Boiling Point [1] ^{o}C	Melting Point [1] ^{o}C	Flash Point [1] ^{o}C	Liquid Density [2] kg/m^3	Vapour Density [3] kg/m^3	Auto-igniti Temp. [1] ^{o}C	Flammable Limits % by vol in air	Lower Explosion Limit (LEL) %	Upper Explosion Limit (UEL) %	LC $_{50}$ In air/ water mg/m^3	MAC Value mg/m^3	LD$_{50}$ Oral [4] g	Chemical Reactivity	Notes
Ammonia	Ammonia	NH_3	17.031	L	38.0	-58.0	n.a.	380.4	0.596	651.0	16-25	15.0	30.2	2000	14	350		(2),(5)
Anthracene	Anthracene	$C_{14}H_{10}$	178.23	S/L/V	340	127	121	1280	6.15	540	n.a.-n.a.	0.6	n.a.	170	n.a.	2700		
Benzene	Benzene	C_6H_6	78.11	V	80	5.5	-11	876.5	2.77	580	n.a.	1.2	8	31951	3.25	930		
t-butanol	Ter-butyl alcohol	$C_4H_{10}O$	74.1	L/V	83	25	11	800	2.6	470		2.3	8			300		
Carbon	Carbon	C	12.011	S	**3825**	**4492**		2200										
Chlorine	Chlorine	Cl_2	70.9	V	-34.6	-102	n.a.		2.5	n.a.	n.a.	n.a.	n.a.	849	3	293 ppm		
Hydrochloric acid	Hydrochloric acid	HCl	36.5	L/V	108	-50	n.a.	1033		n.a.	n.a.	n.a.	n.a.	4655	25	n.a.		
Carbon monoxide	Carbon Monoxide	CO	28.01	V	-191.5	-205	n.a.	1145	0.96	605	125.5-74.2	12.4	75	3760 ppm	29	n.a.		
Carbon dioxide	Carbon dioxide	CO_2	44.01	V	-78.4	-56.57	n.a.	1799	1.522		n.a.	n.a.	n.a.	n.a.	9000	n.a.		
m-Cresol	3-methyl benzenol	C_7H_8O	108.11	S/L/V	202	11	81	1050	3.72	555	n.a.	1.3	n.a.	29	n.a.	121		
Fluorene	Fluorene	$C_{13}H_{10}$	166.22	S/L/V	295	114.8	151	1203		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		
Hydrogen	Hydrogen	H_2	2.016	V	-252.87	-259.34		820	0.07	560	n.a.	4	76	n.a.	n.a.	n.a.		
Hydrogen sulphide	Hydrogen sulphide	H_2S	34.08	V	-59.55	-85.5	-82.4	1393	1.189	260	4-75	4.3	46	712 ppm	15	n.a.		
Indene	Indene	C_9H_8	116.16	S/L/V	182	-1.8	56	996		n.a.	n.a.	n.a.	n.a.	14000	45	2300		
Methane	Methane	CH_4	16	V	-162	-182	-221	422.62	0.55	537	**5-15.4**	4.4	16	14	n.a.	n.a.		
Naphtalene	Naphtalene	$C_{10}H_8$	128.17	S/L/V	217.9	80.2	79	1025.3	4.42	526	0.9-5.9	0.9	5.9	large	50	n.a.		
Nirogen dioxide	Nitrogen dioxide	NO_2	46.006	V	21.15	-9.3	n.a.	1880	1.58	n.a.	n.a.	n.a.	n.a.	115 ppm	4	n.a.		
Nitrogen	Nitrogen	N_2	28.013	V	-195.79	-210.06	n.a.	1145	0.96	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		
Nitric oxide	Nitrogen monoxide	NO	30.006	V	-151.74	-163.6	n.a.	1226	1.036	n.a.	n.a.	n.a.	n.a.	n.a.	30	350 ppm		
Oxygen	Oxygen	O_2	31.999	V	-182.95	-218.79		1308	1.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		
Phenol	Hydroxy benzene	C_6H_6O	94.11	L/V	181.8	40.9	78	1096.7	3.2	605	1.5	1.3	9.5	316	8	319		
Pyrene	Pyrene	$C_{16}H_{10}$	202.26	S/L/V	404	151.2	n.a.	1271		n.a.	n.a.	n.a.	n.a.	100000	n.a.	2700		
Pyridine	Pyridine	C_5H_5N	79.1	S/L/V	115.2	-41.6	17	981.9	2.7	550	1.8-12.4	1.8	12.4	21000 ppm	0.9	891		
Sulphur	Sulphur	S	32.066	S/L/V	444.6	115.21	195	2070		235	n.a.	n.a.	n.a.	1660	n.a.	8437		
Toluene	Methyl benzene	C_7H_8	92.14	S/L/V	111	-95	4	836.6	3.2	480	n.a.	1.2	7	49000	150	636		
Water	Water	H_2O	18.02	L/V	100	0	n.a.	997			n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		

Notes:

[1] At 101.3 kPa

[2] Density at 25 ^{o}C, unless specified otherwise

[3] At 0 ^{o}C

[4] Oral ingestion in (g) for a male of 70kg weight

[5] Density at -47 ^{o}C from H_2O at 4 ^{o}C

[6] Density at -45 ^{o}C from H_2O at 4 ^{o}C

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*Converting mg/m3 -->ppm & vice versa: mg/m3 to ppm calculator

Appendix 1-12: Membrane appendix

Membranes have found many different applications in chemical engineering. This chapter is a small introduction to membrane processes. First the different membrane processes will be described, after which the processing with membranes is further described.

Processes

The following membrane processes that are most common in the chemical industry: Microfiltration, ultrafiltration, nanofiltration, reverse osmosis, gas permeation, pervaporation, pertraction. These processes will be described below.

Micro-filtration, Ultra-filtration, Nano-filtration

Micro-filtration, ultra-filtration and nano-filtration can be regarded as sieves with really small pores. Micro-filtration operates in the range of 0.1-10 μm, and ultra-filtration separates particles that are larger than 0.001-0.15 μm from the bulk. (Seckler et al., 2004) The smaller the particles to be separated, the higher the needed pressure for adequate separation. The pressures needed for micro-filtration range from 100 to 500 kPa, whereas ultrafiltration is operated at a pressure of 100-800 kPa. (Drioli, Giorno, 1999)

Reverse osmosis

Normal osmosis occurs when two solutions with different concentrations are connected through a semi-permeable membrane. The concentration difference causes the solvent to flow to the solution with the highest concentration in order to decrease the difference in chemical potential caused by the concentration difference. The pressure difference associated with this process is called the osmotic pressure. When a pressure is applied to the more concentrated solution that is larger than the osmotic pressure, the solvent will flow in the direction of the clearer solution. Therefore the driving force in this process is the difference between the applied pressure and the osmotic pressure.

Gas permeation

Gas permeation is a method for separating a gaseous mixture into two streams of different compositions. The separation can take place because the transport through the membrane is controlled by the affinity of the membrane for the different components. The difference in permeation rates then causes the separation to take place (Savelski, 2004).

Pervaporation

In pervaporation volatile compounds of a mixture are selectively evaporated from the feed. This makes it a combination of membrane permeation and evaporation (Kumar, 2002).

Pertraction

Pertraction, like pervaporation, is a combination of two conventional processes. In this case extraction is combined with separation of the extractant. Since the extractant and the feed are on the opposite sides of the membrane, the extractant does not have to be removed from the feed, while the unwanted compounds diffuse into the extractant phase.

Operational considerations

Material

Membranes are usually made of polymers or ceramics. There is also a difference between dense and porous membranes. The porous membranes are usually inorganic. Table 1 lists a number of polymers and their applications in the membrane processes discussed above. The abbreviations of the processes are as follows:

MF	micro-filtration
UF	ultra-filtration
NF	nano-filtration
RO	reverse osmosis
GS	gas permeation
PV	pervaporation

Table 1. Polymer materials for membranes (adapted from Drioli (1999)

	MF	UF	NF/RO	GS	PV
Cellulose acetate	x	x	x	x	x
Cellulose triaceate	x	x	x		
Blend CA/triacetate			x		
Cellulose esters	x				
Cellulose nitrate	x				
Blend CA/CN	x				
Poly(vinyl alcohol)	x				
Polyacrylonitrile		x			x
Poly(vinyl chloride)	x				
PVC copolymer	x	x			
Acrylic copolymer	x				
Aromatic polyamide	x	x	x		
Aliphatic polyamide	x	x			
Polyimide	x	x	x	x	
Polysulfone	x	x			
Sulfonated polysulfone		x	x	x	
polyether-ether-ketone (PEEK)	x	x			
Polycarbonate	x				
Polyester	x				
Polypropylene	x				x
Polyethylene	x				x
Polytetrafluoroethylene (PTFE)	x	x			x
Poly(vinylidene difluoride) (PVDF)	x	x			x
Collagen					x
Chitosan					x
Zeolites				x	x
Polyorganophosphazene				x	x
Polydimethylsiloxane (PDMS)				x	x

Mode of operation

There are four modes of operation. Perfect mixing, countercurrent, co-current, and cross flow. Figure 1 gives a graphical interpretation of the modes of operation.

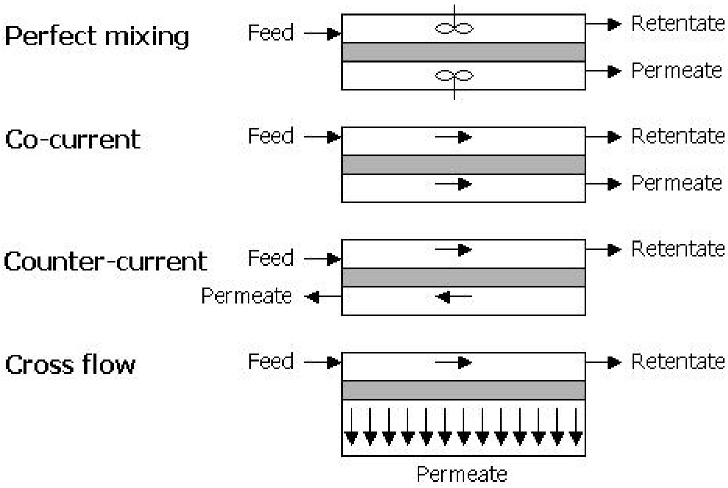


Figure 1. Modes of operation of membrane processes (adapted from Seckler, 2004)

Modules

Membranes can have three configurations. The membranes can be flat, tubular, or hollow fibres. In the flat configuration, sheets membrane are stacked or wound up. This maximises the available surface area per cubic meter. When the membranes are tubular, small tubes are put parallel and usually the feed flows inside the membrane, and the retentate is on the outside of the membrane. The difference between tubular membranes and hollow fibre membranes is that hollow fibre membranes touch, whereas the is a distance between tubular membranes.

Appendix 1-14: Background to Aspen calculations

Aspen Plus was used to model a gasification process. Aspen can calculate both thermodynamic equilibria and reaction kinetics. Here, only the thermodynamics were modelled, because handling kinetics properly is quite difficult. On the next page one can find the Aspen flow sheet. A description is given below.

The actual model

First the wood is crushed from chips having an average diameter (surface-volume sphere) of 2 cm to particles with an average of 5 mm. This milled wood is fed to a RYield reactor.

The RYield reactor decomposes the wood to the separate pure substances, H_2, O_2, C, Cl_2, N_2, S etc. Then, a Gibbs reactor calculates the thermodynamic equilibrium. This result did not match the references [Brage, C.,1996, De Jong 2003, Den Uil 2004, Hastaoglu 1995, Heller 2004, Matsamuraa 2004, Mochidzuki 2002, Mozaffarian 2004, Schröder 2004, , Ibarra 1991, Li AM 1999, Sharma 2003, Wagenaar 1994, Yu, Q., [1997], Zabaniotou 1994] as kinetics were not taken into account. These were investigated later. In fact, Aspen gives quite an idealistic picture, the maximum that could be reached when time is no major player. The RGIBBS reactor is also fed with steam and air, and so will the real reactor. After the RGibbs reactor, ashes and other solids have to be separated, tar has to be scrubbed from the gaseous stream and also water has to be removed and fed back. However, in Aspen no tar was being created as Aspen only gives the thermodynamic equilibria, but in the real case there is.

In the reactor a grid on the bottom of the bed will separate large, non-fluidisable ash particles from the reactor. This is ‘simulated’ in Aspen by the solid splitter and the screen. Fly-ash is taken out to in Aspen, but to be realistic these small particles are mixed again with the gas stream and removed by cyclones and a bag-filter.

The data
The most important data needed to build the model are given below.

STREAM CLASS	MCINCPSD
PROPERTY METHOD	RK-ASPEN
WOOD	NON CONVENTIONAL
TAR	MIX OF SEVERAL AROMATICS
ENTHALPY MODEL	HCOALGEN
DENSITY MODEL	DCOALIGT
HCOALGEN	6-1-1-1
HCOMB	20980088.9 J/kg

Further data are provided in APEEEENIZ ???B. (de aspentekstfile)

The table should be read as follows: In Aspen difficult solids like coal and wood are modelled using the NON-CONVENTIONAL component properties. Aspen has a few Coal based models included, but these can be modified according to the exact type of coal a company may have. It appeared to be possible to adapt the coal model for wood, as they have some things in common. In the table the chosen coal models are reported. Changing these for the char-models or Coal-8 models didn't change the results. Now the heat of combustion of wood could be entered, provided that one changes the first 1 of the HCOALGEN model to a 6 in order to enter custom values.

Next, the so-called ULTANAL, PROXANAL and SULFANAL values had to be entered. These represent the CHO-composition, the moisture (gas, liquid, solid) content and sulpfur content. Values were obtained from Turn [YEAR], Li [2004], Greg, Raoa [2004], Heller [2004], Lv, Mochidzuki and Fan, see also APPENDIC Excelbestand and aspenfile.

Ash was also modelled as a non-conventional solid. However, not much needed to be changed, as Aspen 'knows' how to deal with ash when it is combined with the coal model.

Tar was more difficult. Based on literature (Brage, Yu, Schröder and Wagenaar [1994]) the average composition of tar was chosen APPENDX. Ten substances were selected to represent tar. These were benzene, phenol, kresol, indene, naphtalene, pyrene, anthracene, toluene, fluorene and pyridine.

Both prof. Moulijn and ir. De Jong approved this way of modelling.

==

Using the density and enthalpy models for coal (when this density model was switched for the char model, no significant differences were obtained and so didn't the other coal model) it was possible to model wood.

Many sources describe different processes, using different reactors. First it was necessary to calculate the thermodynamics. Therefore a yield reactor was chosen and the approximate yields were searched for in the journals. (Chaudhari 2003, Feng 2004, Fiaschi 2001, Franco 2003, Fushimi 2003, Li 2004, Lv 2003, Lv 2004a, Lv 2004b, Prins 2003, Raoa 2004, Schuster 2001) – [kinetiek].

From these data, which differed quite a lot, the composition of 'tar' was chosen, as can be found in the data appendix adjusted with the ASPEN model (Brage, Yu, Schröder and Wagenaar).

The FLOW IN, Wood, could be specified in ASPEN, making use of special models for nonconventional solids. This means that the CHONSCl values (ULTANAL) and the GLS percentages have to be entered (PROXANAL). For this (Turn, Li 2004, Greg, Raoa 2004 , Heller 2004, Lv, Mochidzuki and Fan were consulted).

Before it has already been stated that the models for coal were used, more precisely, the HCOALGEN and DCOALIGT. The enthalpy model (HCOALGEN) was modified for wood (6-1-1-1; HCOMB 20980088.9 J/kg). This way of defining wood was supported by prof. Moulijn and ir. W. de Jong.

Fermentation modelling in Aspen

After the gasification with all its equipment the fermentation is modelled in Aspen. The fermentation is modelled as two RYield reactors. The first reactor represents the growth reactor, in this reactor bacteria are breed, which will be used later in the actual production fermentor. The production reactor is also modelled with RYield reactor. The reactors are fed with the syn-gas from the gasification and with additional water and air. The second RYield reactor actually represents three reactors, which are linked together.

A quarter of the amount of produced syn-gas is fed to the first reactor., the other three quarters are fed to the secondary reactor. The total syn-gas stream is split into two streams with a standard split unit. The same is done with the water stream needed for the total fermentation. The necessary amounts of water come from the calculations made in Matlab. The yields of the reactors are determined by the amount of bacteria PHB are produced, and the amounts of air and syn-gas, which are consumed.

PHB and bacteria are defined in Aspen as non-conventional solids. The general model for non-conventional solids is used and values for the density, heat of combstion and heat of formation are filled in. These values can be defined at pure-component sheets. In the following table can the values be found, which are used.

	Heat of Combustion [J/(kg·K)]	**Heat of formation [J/kg]**	**Density [kg/m^3]**
PHB	1400	0	1250
Bacteria	1400	0	1400

The following values are filled in to produce Bacteria and PHB, based on the calculation of fermentation made in Matlab.

	Reactor 1	**Reactor 2**	**Inerts**
Bacteria	0.0605	0.0605	Water
Oxygen	0.9006	0.9006	Carbon dioxide
Hydrogen	0.0009	0.0009	Nitrogen
Carbon monoxide	0.0380	0.0380	Hydrogen Sulfide
			Hydrogen Chloride
			Ammonia
			Bacteria

After the reactors the gases are split from the effluent of the reactor, because in reality the gases are also separated from the fermentation broth. For this purpose SEP units are used, all the gases are split from the liquid, so the liquid can further be processed.

Aspen model development for DSP

a. Introduction

Within the context of numerically analysing the downstream processing section an Aspen model was developed. The model was developed to achieve the following objectives:

1. To explore the options for solvent regeneration in the DSP section.
2. To produce a complete set of mass and heat balances, which could be used to dimension the equipment.
3. To produce a process flow sheet for the downstream processing section.

A diagram of the model is contained in appendix 1-13.

b. Model development strategy

The model was developed in three stages. Firstly a model was constructed with no internal recycle streams, this was necessary as the introduction of recycle streams makes analysis of a model complicated and the estimation of initial values almost impossible. This model was also used to arrive at a concrete concept for the downstream process as it demonstrated the possibility to separate water from t-butanol using a relatively simple distillation apparatus. This model was used to produce initial estimates for the stream sizes and also to perform an initial optimisation of the stripper section.

The second step was to see whether solids could also be successfully added to the model, this was necessary to achieve the second stated goal. From the development of the gasifier it was already known within the group that Aspen was capable of modelling streams consisting of solids and liquids.

Finally the internal recycle streams were closed. This was carried out to arrive at estimates for the performance of the complete process concept.

c. Phase 1: No solids, no recycles

PHB enters the DSP sub process in an intracellular form, this results in water entering the system. Inevitably this water has to be removed. Aspen was therefore used to examine the ability to separate t-butanol from water using a distillation column.

The first observation was that a suitable thermodynamic model for a mixture of t-butanol and water was hard to find. Many of the models typically used for modelling of polar liquid mixtures produced entirely meaningless phase equilibria. However after trying numerous potential candidates the NRTL-2 model was found to be suitable.

An example of the resulting phase equilibria encountered during stripping can be found in appendix ??? From this diagram it is clear that water and t-butanol form an azeotropic mixture at a water mass fraction of approximately 0.15. To the right of this azeotrope a broad region is found with excellent potential for separation by distillation. From this diagram it is also clear that the region within which it is possible to operate is a water mass fraction between 0.18 and 1.0. This region easily encompasses the compositions found in the proposed process.

On the basis of this model virtually complete recovery of t-butanol could be achieved using a stripper with 9 equilibrium stages. The required rate of steam of addition to the stripper was also determined to be of the order of 300 kg/hour.

d. Phase 2: Addition of solids, no recycles

Having succeeded in achieving a reasonable performance for solvent recovery the next step was to investigate the possibilities to include solids in the model. This was achieved by defining two non-standard solid components for PHB and cell debris. This was carried out as described in the document ‘Getting started with solids’[Luc&MrT???] and enabled the solids to be included in the heat balance.

Aspen treats solids as a separate sub stream from liquids. For this reason it is not possible to define the composition of an entire stream in terms of the mass fraction of all elements combined, liquids are defined separately from solids. In addition it is not possible to define the PSD (particle size distribution) of two solid components independently in one stream, hence if two solids with different sizes are to be used then they have to be defined as to separate feeds and mixed. This makes working with solids much more complicated than with only liquids.

At this point it must be stated that Aspen 11.1 is not designed with bio-separations in mind. The smallest particles it accepts must be at least 1 micron in size. This is larger than the anticipated PHB granule size. In addition all the units for solid-liquid processing provided by Aspen are intended for processing solids of a much larger size, such as coal dust. As a result the solids had to be recovered using ideal separators.

For this reason the only advantage gained by adding solids was a complete mass and heat balance for both liquids and solids. The main conclusion is that solid streams can only be accurately modelled in Aspen if they have a particle diameter of at least a few hundred microns.

e. Phase 3: Complete model

The final step was to close the material cycles where possible by introducing mixers and splitters. MIX2 accepts the recycle stream of t-butanol rich solvent leaving the top of the stripper. SPLIT1 takes a fraction of the water rich stream from the bottom of the stripper and recycles it to the reboiler.

f. Description of streams and units

The Aspen model consists of units attached to each other by means of material streams. The characteristics and purpose of each stream and unit is described below and proceeds from left to right as shown in appendix ???:

Process inputs

Four streams enter on the left of the diagram, these are:

Table 1: Process inputs

Stream	Description
TBUT-IN	The makeup stream of t-butanol entering the process, this is to replace any t-butanol lost.
PHB-IN	This is the mass flow of PHB entering the process
H2O-IN	This is water entering the process with the cells
DEBRI-IN	This is the stream of cell debris which contaminates the PHB

The last three streams in Table 1 are combined in the unit M1-DSP to form a material stream with the same composition as a cell suspension. This is not a real unit, it is simply a method to create ‘cells’.

Blending point

The cell suspension, t-butanol makeup feed and solvent recycle stream are mixed, at point M2-DSP, to form a single suspension of cells in a solvent with the appropriate composition. This is the stream CELLS-LP, where LP stands for low pressure (1 bar).

Homogeniser section

The cell suspension is now ready to be homogenised. This task is simulated by the units P1-DSP and R1-DSP (the homogenisation unit). The unit P1-DSP increases the pressure to 400 bar, yielding the stream CELLS-HP. The cell suspension is then passed through the unit R1-DSP (which is no more than a valve, as in reality) to yield a suspension of PHB and cell debris, this is the stream PHPSUSPE. At this point the pressure is once more 1 bar.

PHB recovery

At this point PHB is recovered. As outlined in chapter ??? this occurs by centrifugation with the unit S1-DSP. The PHB recovered leaves in the stream RAWPHB. The remaining liquid, which is a suspension of cell debris, leaves S1-DSP in the stream DEBSOLV.

Solvent regeneration and debris precipitation

The stream of solvated debris, DEBSOLV, now enters the stripper unit, C1-DSP. The function of this unit is to remove t-butanol from the liquid phase. This is achieved by counter-current contacting with steam, supplied by the stream STEAM. At the same time the solubility of the debris will decrease resulting in precipitation. The vapour stream leaving the top of the stripper contains virtually all the t-butanol which enters the unit and is hence called TBUTRICH. The stream leaving the bottom of the unit consists almost entirely of water and cell debris and is called DEBR-H2O.

Debris recovery

The water stream, contaminated with cell debris, is purified by means of filtration (S2-DSP). Hence the stream DEBR-OUT contains the debris leaving the process and the other stream is called H2O.

Recycle streams

Then the two recycle streams remain. A fraction of the water leaving the process is recycled in the stream H2O-REC to the steam generation unit E2-DSP. The t-butanol stream TBUTRICH enters E1-DSP where it is cooled to become the stream SOLV-REC, which returns to the beginning of the process.

Appendix 1-15: Air separation techniques

Adsorption

Oxygen can be separated from nitrogen because some materials adsorb nitrogen. The spaces in zeolites contain an electrostatic field that causes nitrogen to be adsorbed better than oxygen, because nitrogen is more polarisable. [Smith 2002]
A second separation technique that is based on adsorption is the use of carbon molecular sieves. Carbon molecular sieves (CMS) have pores in the molecular range. Because oxygen molecules are smaller than nitrogen, oxygen can diffuse through the pores in a higher rate than nitrogen. [Tan 2004]
Pressure-swing adsorption based on the preference of the adsorbent to contain nitrogen. Pressurised air is led over an adsorption bed until the bed is fully saturated. The air feed is then switched to another unit, while the first unit is regenerated by either temperature increase, or pressure change. These steps are necessary to reverse the adsorption equilibrium. Oxygen purity ranges from 93 to 95%. The bed volume mainly determines the cost of this process. Figure 1 shows a schematic of pressure-sing adsorption.

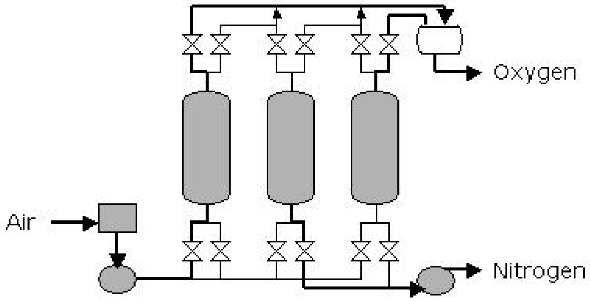


Figure 1. Adsorption-based separation process. Adapted from Smith [2001]

Chemical

Chemical processes use the characteristics of some molten salts to absorb and desorb oxygen at different conditions. For these processes a proper pretreatment is needed, because carbon dioxide and water break down the salt. Figure 2 shows an example of a chemical air separation process. Air is compressed to about 13 bar prior to the pretreatment. The desorption takes place at 650 ºC.

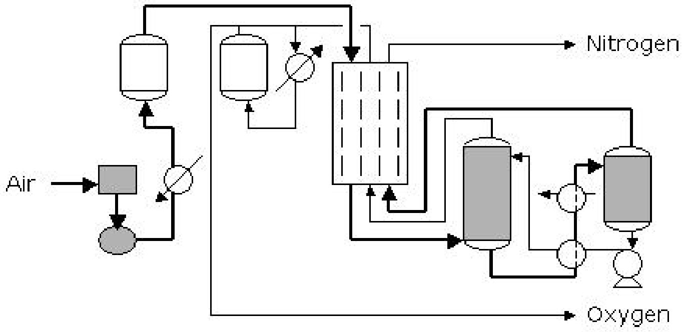


Figure 2. Chemical air separation process. Adapted from Smith [2001]

Membrane

Membrane separation is based on the difference in permeability of the species to be separated. Oxygen is a smaller molecule and will therefore permeate faster than nitrogen. Figure 3 shows a drawing of a typical membrane process.

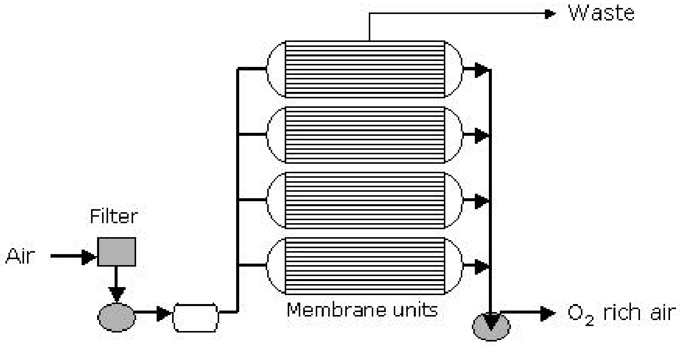


Figure 3. Polymeric membrane air separation process. Adapted from Smith [2001]

Many different membrane configurations exist. In Appendix **???** membranes are discussed in more detail. Product purity is about 40 vol-% oxygen. [Smith 2001]

Oxygen separation can also be done by using ceramic materials. These ceramic membranes are also called ion transport membranes. Oxygen is ionised at the surface of the membrane, where it is transported over the membrane under the influence of an applied electric voltage or partial pressure difference. Upon leaving the membrane on the other side, the oxygen is reformed. Nearly pure oxygen can be produced using this process. A simple schematic is depicted in Figure 4.

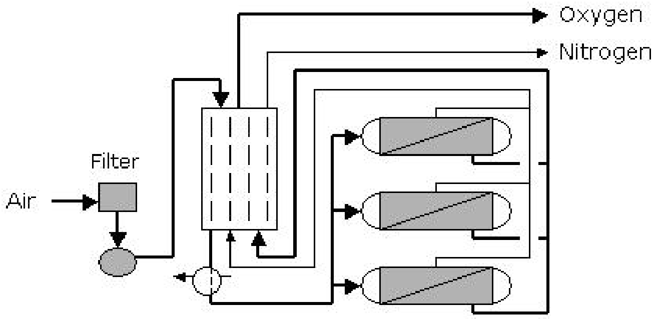


Figure 4. Ion transport membrane air separation process. Adapted from Smith [2001]

Cryogenic distillation

Cryogenic distillation is most useful for large scale operation. Figure 5 shows the unit operations that are necessary for cryogenic separation.

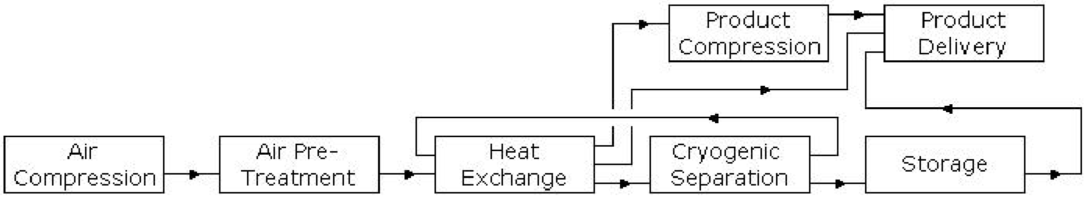


Figure 5. Unit operations fot a cryogenic air separation process. Adapted from Smith [2001]

From the processes described above the most suitable option would be to use a membrane unit. However, the purity obtained from membrane separation is not high enough to justify its costs. Therefore enriched air is not an option in our process.

PROCESS STREAM SUMMARY

STREAM Nr. :		1	IN	2		3		4		5	
Name :		Wood feed		Grinded wood		LP wood		MP wood		Product gas	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02									2.00E-02	0.0099206
Methane	16.00										
Water	18.02									5.26E-01	0.0291898
Carbon mono	28.01									0.214	0.0076401
Carbon dioxi	44.01									0.257	0.0058396
Oxygen	31.99										
Nitrogen	28.01									0.577	0.0205976
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00	0.431	0.0004259	0.431	0.0004	0.431	0.0004	0.431	0.0004		
Ash											
PHB											
Bacteria											
Total		0.43	0.0004	0.43	0.0004	0.43	0.0004	0.43	0.0004	1.59	0.0732
Enthalpy	kW	-3189		-3189		-3189		-3189		-6036	
Phase	L/V/S	S		S		S		S		V	
Press.	Bara	1.0		1.0		1.0		5.0		5.0	
Temp	oC	25.0		25.0		25.0		25.0		1537.3	

STREAM Nr. :		6		7		8		9		10	
Name :		Effluent E01		Effluent E02		Effluent E03		Effluent S01		Effluent S02	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02	2.00E-02	0.0099	2.00E-02	0.0099	2.00E-02	0.0099	2.00E-02	0.0099	2.00E-02	0.0099
Methane	16.00										
Water	18.02	5.26E-01	0.0292	5.26E-01	0.0292	5.26E-01	0.0292	5.26E-01	0.0292	5.26E-01	0.0292
Carbon monoxic	28.01	0.214	0.0076	0.214	0.0076	0.214	0.0076	0.214	0.0076	0.214	0.0076
Carbon dioxide	44.01	0.257	0.0058	0.257	0.0058	0.257	0.0058	0.257	0.0058	0.257	0.0058
Oxygen	31.99										
Nitrogen	28.01	0.577	0.0206	0.577	0.0206	0.577	0.0206	0.577	0.0206	0.577	0.0206
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		1.59	0.0732	1.59	0.0732	1.59	0.0732	1.59	0.0732	1.59	0.0732
Enthalpy	kW	-6566		-7809		-8005		-8005		-8005	
Phase	L/V/S	V		V		V		V		V	
Press.	Bara	5.0		5.0		5.0		5.0		5.0	
Temp	oC	1366.2		950.6		883.6		883.6		883.6	

STREAM Nr. :		11		12		13		14		15	
Name :		Dried gas		Compressed syngas		Feed R02		Syngas		Bacteria R02	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02	2.00E-02	0.0099	2.00E-02	0.0099	0.0050	0.0025	1.50E-02	0.0074		
Methane	16.00										
Water	18.02	1.20E-02	0.0007	1.20E-02	0.0007	0.0030	0.0002	9.00E-03	0.0005	2.35E-01	0.0147
Carbon mono	28.01	0.214	0.0076	0.214	0.0076	0.0535	0.0019	1.61E-01	0.0057		
Carbon dioxi	44.01	0.248	0.0056	0.248	0.0056	0.0620	0.0014	1.86E-01	0.0042		
Oxygen	31.99										
Nitrogen	28.01	0.576	0.0206	0.576	0.0206	0.1440	0.0051	4.32E-01	0.0154		
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria										0.012	
Total		1.07	0.0444	1.07	0.0444	0.27	0.0111	0.80	0.0333	0.25	0.0147
Enthalpy	kW	-3194		-3194		-799		-2396		-3666	
Phase	L/V/S	V		V		V		V		L	
Press.	Bara	5.0		5.0		5.0		5.0		5.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr. :		16		17		18		19		20	
Name :		Feed R03		Syngas 2		Bacteria R03		Feed R04		Bacteria R04	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02	0.0050	0.0025	1.00E-02	0.0050			0.0050	0.0025		
Methane	16.00										
Water	18.02	0.0030	0.0002	6.00E-03	0.0003	0.238000	0.0132	0.0030	0.0002	0.241000	0.0134
Carbon monoxi	28.01	0.0535	0.0019	1.07E-01	0.0038			0.0535	0.0019		
Carbon dioxide	44.01	0.0620	0.0014	1.24E-01	0.0028			0.0620	0.0014		
Oxygen	31.99										
Nitrogen	28.01	0.1440	0.0051	2.88E-01	0.0103			0.1440	0.0051		
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB						0.0122				0.0244	
Bacteria						0.0122				0.0122	
Total		0.27	0.0111	0.54	0.0222	0.26	0.0132	0.27	0.0111	0.28	0.0134
Enthalpy	kW	-799		-1598		-3663		-799		-3660	
Phase	L/V/S	V		V		L		V		L	
Press.	Bara	5.0		5.0		5.0		5.0		5.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr. :		21		22		23		24		25	
Name :		Feed R05		Bacteria R05		Discharge P04		Cells		Diluted cells	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02	0.005	0.0025								
Methane	16.00										
Water	18.02	0.003	0.0002	0.244	0.0135	0.244	0.0135	0.064	0.0036	0.314	0.0174
Carbon mono	28.01	0.054	0.0019								
Carbon dioxi	44.01	0.062	0.0014								
Oxygen	31.99										
Nitrogen	28.01	0.144	0.0051								
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10									0.163	0.0022
Wood	1012.00										
Ash											
PHB				0.037		0.037		0.036		0.035	
Bacteria				0.012		0.012		0.012		0.012	
Total		0.27	0.01	0.29	0.01	0.29	0.01	0.11	0.00	0.52	0.02
Enthalpy	kW	-799		-3848		-3848		-1016		-5693	
Phase	L/V/S	V		L		L		L		L	
Press.	Bara	5.0		5.0		5.0		5.0		1.0	
Temp	oC	40.0		40.0		40.0		40.0		63.8	

STREAM Nr. :		26		27		28		29		30	
Name :		Destroyed cells1		Destroyed cells2		PBH S04		Effluent M03		Discharge P07	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.314	0.0174	0.314	0.0174	0.022	0.0012	0.059	0.0033	0.059	0.0033
Carbon monoxi	28.01										
Carbon dioxide	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulphi	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10	0.163	0.0022	0.163	0.0022	0.011	0.0001	0.175	0.0024	0.175	0.0024
Wood	1012.00										
Ash											
PHB		0.036		0.036		0.036		0.036		0.036	
Bacteria		0.012		0.012		0.001		0.001		0.001	
Total		0.53	0.02	0.53	0.02	0.07	0.00	0.27	0.01	0.27	0.01
Enthalpy	kW	-5693		-5680		-398		-1748		-1748	
Phase	L/V/S	L		L		L		L		L	
Press.	Bara	1.0		1.0		1.0		1.0		1.0	
Temp	oC	66.7		69.5		69.5		69.5		69.5	

STREAM Nr.	:	31		32		33	OUT	34	IN	35	IN
Name	:	PHB S05		Discharge P08		PHB product		Sand feed		Methane feed	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.004	0.0002	0.004	0.0002						
Carbon mono	28.01										
Carbon dioxi	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10	0.012	0.0002	0.012	0.0002						
Wood	1012.00										
Ash											
PHB		0.035		0.035		0.035					
Bacteria		0.001		0.001		0.001					
Total		0.05	0.00	0.05	0.00	0.0360					
Enthalpy	kW	-120		-120		149					
Phase	L/V/S	L		L		S					
Press.	Bara	1.0		1.0		1.0					
Temp	oC	70.0		70.0		98.0					

STREAM Nr.	:	36		37	IN	38		39		40	
Name	:	Discharge K01		Air feed		Discharge K02		Air feed fermentation		Air feed E01	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02										
Carbon monoxi	28.01										
Carbon dioxide	44.01										
Oxygen	31.99			0.75046	0.0235	0.75029	0.0235	0.58	0.0180	0.175	0.0055
Nitrogen	28.01			2.47154	0.0882	2.47171	0.0882	1.90	0.0677	0.575	0.0205
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulphi	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total				3.22	0.11	3.22	0.11	2.47	0.09	0.75	0.03
Enthalpy	kW			213		213		30		183	
Phase	L/V/S			V		V		V		V	
Press.	Bara			1.0		5.0		5.0		5.0	
Temp	oC			25.0		40.0		40.0		40.0	

STREAM Nr.	:	41		42	IN	43		44		45	
Name	:	Air feed R01		Water Feed		Discharge P01		Feed water E02		Effluent E02	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02			0.056	0.0031	0.056	0.0031	4.09E-01	0.0227	4.09E-01	0.0227
Carbon mono	28.01										
Carbon dioxi	44.01							0.006	0.0001	0.006	0.0001
Oxygen	31.99	0.175	0.0055								
Nitrogen	28.01	0.575	0.0205					0.001	0.0000	0.001	0.0000
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.75	0.03	0.06	0.00	0.06	0.00	0.42	0.02	0.42	0.02
Enthalpy	kW	716		-882		-882		-6524		-4954	
Phase	L/V/S	V		L		L		L		V	
Press.	Bara	5.0		1.0		1.0		1.0		1.0	
Temp	oC	900.0		25.0		25.0		40.0		360.0	

STREAM Nr.	:	46		47	OUT	48	OUT	49	OUT	50	
Name	:	Feed steam R01		Effluent bottom ash		Effluent fly ash		Effluent tar products		Recycle water	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	4.09E-01	0.0227							3.53E-01	0.0196
Carbon monoxic	28.01										
Carbon dioxide	44.01	0.006	0.0001							0.006	0.0001
Oxygen	31.99										
Nitrogen	28.01	0.001	0.0000							0.001	0.0000
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash				0.002		1.00E-06		1.41E-05			
PHB											
Bacteria											
Total		0.42	0.02	0.00		0.00		0.00		0.36	0.02
Enthalpy	kW	-4954		-1391		1		1		-5640	
Phase	L/V/S	V		S		S		S		L	
Press.	Bara	5.0		5.0		5.0		5.0		5.0	
Temp	oC	722.3		1537.3		884.6		884.6		40.0	

STREAM Nr.	:	51		52	OUT	53	IN	54	IN	55	
Name	:	Effluent V03		Exit water		Feed nutrients		Feed fermentation water		Discharge P02	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	5.15E-01	0.0286	1.62E-01	0.0090			0.232	0.0129	0.232	0.0129
Carbon mono	28.01	1.00E-03	0.0000								
Carbon dioxi	44.01	0.009	0.0002	0.003	0.0001						
Oxygen	31.99										
Nitrogen	28.01	0.002	0.0001	0.001	0.0000						
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Nutrients						0.0001					
Total		0.53	0.03	0.17	0.01			0.23	0.01	0.23	0.01
Enthalpy	kW	-8222		-2582				-3668		-3668	
Phase	L/V/S	L		L		S		L		L	
Press.	Bara	5.0		5.0		1.0		1.0		1.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr.	:	56		57		58		59		60	
Name	:	Effluent M01		Discharge P03		Air feed R02		Air fermentation		Air feed R03	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.232	0.0129	0.232	0.0129						
Carbon monoxic	28.01										
Carbon dioxide	44.01										
Oxygen	31.99					0.144	0.0045	0.43	0.0135	0.144	0.0045
Nitrogen	28.01					0.474	0.0169	1.42	0.0508	0.474	0.0169
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.23	0.01	0.23	0.01	0.62	0.02	1.85	0.06	0.62	0.02
Enthalpy	kW	-3668		-3668		-1511		21		-1511	
Phase	L/V/S	L		L		V		V		V	
Press.	Bara	5.0		5.0		5.0		5.0		5.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr. :		61		62		63		64		65	
Name :		Air Feed R04 R05		Air feed R04		Air feed R05		Effluent air R02		Effluent syngas R02	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02									3.00E-03	0.0002
Carbon mono	28.01									0.0486	0.0017
Carbon dioxi	44.01									0.062	0.0014
Oxygen	31.99	0.29	0.0090	0.144	0.0045	0.144	0.0045	0.144	0.0045		
Nitrogen	28.01	0.95	0.0338	0.474	0.0169	0.474	0.0169	0.474	0.0169	0.144	0.0051
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		1.24	0.04	0.62	0.02	0.62	0.02	0.62	0.02	0.26	0.01
Enthalpy	kW	14		-1511		-1511		-1511		-801	
Phase	L/V/S	V		V		V		V		V	
Press.	Bara	5.0		5.0		5.0		5.0		10.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr. :		66		67		68		69		70	
Name :		Effluent air R02		Effluent syngas R03		Effluent air R02 R03		Effluent syngas R02 R03		Effluent air R04	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02			3.00E-03	0.0002			6.00E-03	0.0003		
Carbon monoxi	28.01			0.048	0.0017			9.60E-02	0.0034		
Carbon dioxide	44.01			0.062	0.0014			1.24E-01	0.0028		
Oxygen	31.99	0.144	0.0045			0.29	0.0090			0.144	0.0045
Nitrogen	28.01	0.474	0.0169	0.144	0.0051	0.95	0.0338	2.88E-01	0.0103	0.474	0.0169
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.62	0.02	0.26	0.01	1.24	0.04	0.51	0.02	0.62	0.02
Enthalpy	kW	-1511		-528		-105		-424		-1511	
Phase	L/V/S	V		V		V		V		V	
Press.	Bara	5.0		10.0		5.0		10.0		5.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr.	:	71		72		73		74		75	
Name	:	Effluent syngas R04		Effluent syngas		Effluent air		Effluent air R05		Effluent syngas R05	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	3.00E-03	0.0002	9.00E-03	0.0005					3.00E-03	0.0002
Carbon mono	28.01	0.051	0.0018	1.47E-01	0.0052					0.051	0.0018
Carbon dioxi	44.01	0.062	0.0014	1.86E-01	0.0042					0.062	0.0014
Oxygen	31.99					0.432	0.0135	0.144	0.0045		
Nitrogen	28.01	0.144	0.0051	0.432	0.0154	1.422	0.0508	0.474	0.0169	0.144	0.0051
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.26	0.01	0.77	0.03	1.85	0.06	0.62	0.02	0.26	0.01
Enthalpy	kW	-802		-636		-1576		-1511		-611	
Phase	L/V/S	V		V		V		V		V	
Press.	Bara	10.0		10.0		5.0		5.0		10.0	
Temp	oC	40.0		40.0		40.0		40.0		40.0	

STREAM Nr.	:	76	OUT	77	OUT	78	IN	79		80	
Name	:	Exit syngas		Exit air		Feed T-butanol		Discharge P05		Effluent water S03	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	1.20E-02	0.0007							0.179	0.0099
Carbon monoxic	28.01	1.98E-01	0.0071								
Carbon dioxide	44.01	2.48E-01	0.0056								
Oxygen	31.99			5.76E-01	0.0180						
Nitrogen	28.01	5.76E-01	0.0206	1.896	0.0677						
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulph	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10					2.78E-07	0.0000	2.78E-07	0.0000		
Wood	1012.00										
Ash											
PHB										0.001	
Bacteria											
Total		1.03	0.03	2.47	0.09	0.00	0.00	0.00	0.00	0.18	0.01
Enthalpy	kW	-1283		30		1		1		-2832	
Phase	L/V/S	V		V		L		L		L	
Press.	Bara	10.0		5.0		1.0		5.0		5.0	
Temp	oC	40.0		40.0		25.0		25.0		40.0	

STREAM Nr.	:	81	OUT	82		83		84		85	
Name	:	Discharge P13		Effluent S04		Discharge P06		Effluent T-butanol C01		Discharge K05	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.179	0.0099	0.292	0.0162	0.292	0.0162	0.033	0.0018	0.033	0.0018
Carbon mono	28.01										
Carbon dioxi	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10			0.152	0.0021	0.152	0.0021	0.152	0.0021	0.152	0.0021
Wood	1012.00										
Ash											
PHB		0.001									
Bacteria				0.011		0.011					
Total		0.18	0.01	0.46	0.02	0.46	0.02	0.19	0.004	0.19	0.004
Enthalpy	kW	-2832		-5282		-5282		-1063		-1063	
Phase	L/V/S	L		L		L		V		V	
Press.	Bara	5.0		1		1.0		1		1.0	
Temp	oC	40.0		69.5		69.5		98.94		146.3	

STREAM Nr.	:	86		87		88		89		90	
Name	:	Effluent S06		Inflow M03		Effluent water C01		Discharge P09		Inflow S07	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.037	0.0021	0.037	0.0021	0.332	0.0184	0.332	0.0184	0.332	0.0184
Carbon monoxic	28.01										
Carbon dioxide	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulphi	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10	0.164	0.0022	0.164	0.0022						
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.20100	0.00	0.20	0.00	0.33	0.02	0.33	0.02	0.33	0.02
Enthalpy	kW	-1332		-1332		-5168		-5168		-5168	
Phase	L/V/S	V/L		L		L		L		L	
Press.	Bara	1.0		1.0		1.0		1.0		1.0	
Temp	oC	98.8		70.0		100.1		100.1		70.0	

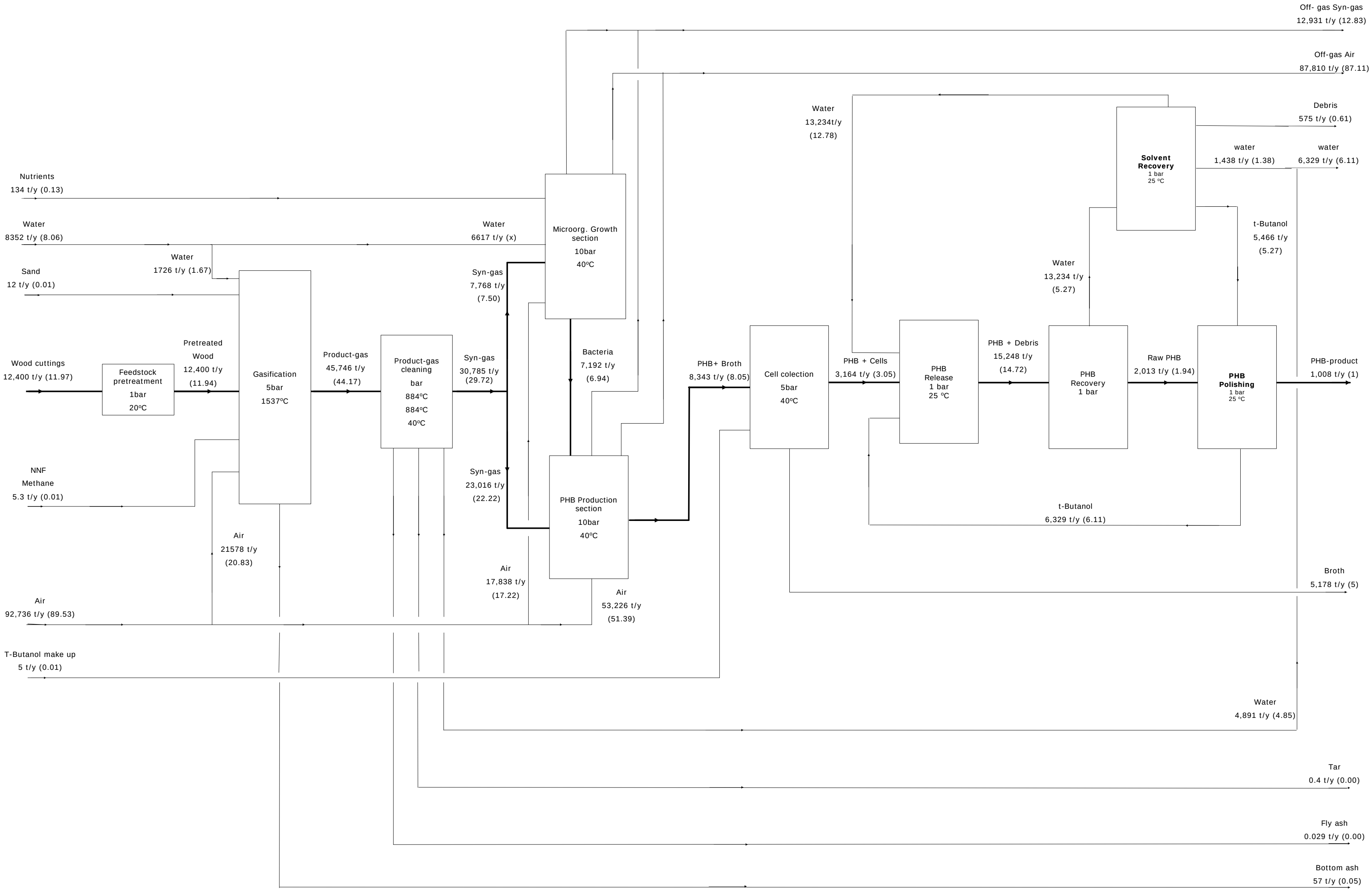
STREAM Nr.	:	91		92		93		94	OUT	95	OUT
Name	:	Effluent water S07		Discharge P10		Effluent debris S07		Outlet debris		Outlet water	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.321	0.0178	0.321	0.0178	0.011	0.0006	0.011	0.0006	0.053	0.0029
Carbon mono	28.01										
Carbon dioxi	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10										
Wood	1012.00										
Ash											
PHB											
Bacteria						0.011		0.011			
Total		0.32	0.02	0.32	0.02	0.02	0.00	0.02	0.00	0.05	0.00
Enthalpy	kW	-4997		-4997		-171		-171		-835	
Phase	L/V/S	L		L		L		L		L	
Press.	Bara	1.0		1.0		1.0		1.0		1.0	
Temp	oC	70.0		70.0		70.0		70.0		70.0	

STREAM Nr.	:	96		97		98		99		100	
Name	:	Inflow E03		Effluent E03		Recycle water 2				Effluent water S05	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.074	0.0041	0.074	0.0041	0.194	0.0108	0.194	0.0108	0.055	0.0031
Carbon monoxic	28.01										
Carbon dioxide	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sulphi	34.08										
Nitric oxide	30.01										
Nitrogen oxide	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric ac	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10									0.163	0.0022
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.07	0.00	0.07	0.00	0.19	0.01	0.19	0.01	0.22	0.01
Enthalpy	kW	-1144		-948		-3048		-3048		-1628	
Phase	L/V/S	V		V		V		L		L	
Press.	Bara	1.0		1.0		1.0		1.0		1.0	
Temp	oC	70.0		300.0		70.0		70.0		69.9	

STREAM Nr.	:	101		102		103		104		105	
Name	:	Inlet P12		Discharge P12		Storage		Inlet water M02			
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00										
Hydrogen	2.02										
Methane	16.00										
Water	18.02	0.249	0.0138	0.25	0.0138			0.25	0.0156		
Carbon mono	28.01										
Carbon dioxi	44.01										
Oxygen	31.99										
Nitrogen	28.01										
Benzene	78.11										
Phenol	94.11										
M-cresol	108.11										
Toluene	92.14										
Indene	116.16										
Fluorene	166.22										
Anthracene	178.23										
Pyrene	202.26										
Naphtalene	128.17										
Hydrogen sul	34.08										
Nitric oxide	30.01										
Nitrogen oxid	46.01										
Sulphur	32.07										
Chloride	70.90										
Hydrochloric	36.50										
Pyridine	79.10										
Ethane	30.11										
Ammonia	17.03										
Tert-butanol	74.10	0.163	0.0022	0.163	0.0022			0.16	0.0002		
Wood	1012.00										
Ash											
PHB											
Bacteria											
Total		0.41	0.02	0.41	0.02			0.41	0.02		
Enthalpy	kW	-4674		-4674				-4674			
Phase	L/V/S	L		L				L			
Press.	Bara	1.0		1.0				1.0			
Temp	oC	70.1		70.1				70.1			

Overall Component Mass Balance and Heat Balance

STREAM Nr.	:	1+34+35+37+42+53+54+78+1		33+47+48+49+52+76+77+81+94+95			
Name	:	Total Plant	IN	Total plant	OUT		IN-OUT
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Carbon	12.00						
Hydrogen	2.02						
Methane	18.02						
Water	16.00	0.29	0.0160	0.417	0.0231		
Carbon monoxic	28.01			0.198	0.0071		
Carbon dioxide	44.01			0.251	0.0057		
Oxygen	31.99	0.75	0.0235	0.576	0.0180		
Nitrogen	28.01	2.47	0.0882	2.473	0.0883		
Benzene	78.11						
Phenol	94.11						
M-cresol	108.11						
Toluene	92.14						
Indene	116.16						
Fluorene	166.22						
Anthracene	178.23						
Pyrene	202.26						
Naphtalene	128.17						
Hydrogen sulphi	34.08						
Nitric oxide	30.01						
Nitrogen oxide	46.01						
Sulphur	32.07						
Chloride	70.90						
Hydrochloric ac	36.50						
Pyridine	79.10						
Ethane	30.11						
Ammonia	17.03						
Tert-butanol	74.10	2.78E-07	0.0000				
Wood	1012.00	0.43	0.0004				
Ash				0.00201511			
PHB				3.60E-02			
Bacteria				1.20E-02			
		0.0001					
Total		3.94	0.13	3.97	0.14	0.02	0.01
Enthalpy	kW	-7525		-7525			
Phase	L/V/S						
Press.	Bara						
Temp	oC						


Off- gas Syn-gas
12,931 t/y (12.83)
Off-gas Air
87,810 t/y (87.11)
Debris
575 t/y (0.61)
water
1,438 t/y (1.38)
water
6,329 t/y (6.11)
Solvent Recovery
1 bar
25 ºC
Water
13,234t/y
(12.78)
t-Butanol
5,466 t/y
(5.27)
Water
13,234 t/y
(5.27)
Nutrients
134 t/y (0.13)
Water
8352 t/y (8.06)
Water
6617 t/y (x)
Microorg. Growth section
10bar
40ºC
Water
1726 t/y (1.67)
Sand
12 t/y (0.01)
Syn-gas
7,768 t/y
(7.50)
Bacteria
7,192 t/y
(6.94)
Wood cuttings
12,400 t/y (11.97)
Feedstock pretreatment
1bar
20ºC
Pretreated
Wood
12,400 t/y
(11.94)
Gasification
5bar
1537ºC
Product-gas
45,746 t/y
(44.17)
Product-gas cleaning
bar
884ºC
884ºC
40ºC
Syn-gas
30,785 t/y
(29.72)
PHB+ Broth
8,343 t/y (8.05)
Cell colection
5bar
40ºC
PHB + Cells
3,164 t/y (3.05)
PHB
Release
1 bar
25 ºC
PHB + Debris
15,248 t/y
(14.72)
PHB
Recovery
1 bar
Raw PHB
2,013 t/y (1.94)
PHB
Polishing
1 bar
25 ºC
PHB-product
1,008 t/y (1)
NNF
Methane
5.3 t/y (0.01)
Syn-gas
23,016 t/y
(22.22)
PHB Production section
10bar
40ºC
t-Butanol
6,329 t/y (6.11)
Air
21578 t/y
(20.83)
Air
17,838 t/y
(17.22)
Air
53,226 t/y
(51.39)
Broth
5,178 t/y (5)
Air
92,736 t/y (89.53)
T-Butanol make up
5 t/y (0.01)
Water
4,891 t/y (4.85)
Tar
0.4 t/y (0.00)
Fly ash
0.029 t/y (0.00)
Bottom ash
57 t/y (0.05)

	Chapter	Subsection	MIN	MAX	ACTUAL	Status	Author(s)	Checkers	Deadline
	Summary		1	1		Final			
	Table of Contents		1	1		Final			
	1. Introduction		2	3		Final			
	2. Process Options & Selection.		3	4		Final			
	2. Process Options & Selection.	Pretreatment				Final			
	2. Process Options & Selection.	Gasification				Final			
	2. Process Options & Selection.	Fermentation				Final			
	2. Process Options & Selection.	DSP				Final			
	2. Process Options & Selection.	Posttreatment				Final			
	2. Process Options & Selection.	Other				Final			
	3. Basis of Design (BOD)		3	4		Final			
	3. Basis of Design (BOD)	i.Description of the design				Final			
	3. Basis of Design (BOD)	ii. Process Definition				Final			
	3. Basis of Design (BOD)	iii. Basic Assumptions				Final			
	3. Basis of Design (BOD)	iv. Economic Margin				Final			
	4. Thermodynamic Properties and Reaction Kinetics		5	7		Final			
	4. Thermo and Reaction Kinetics	a. Operating Window				Final			
	4. Thermo and Reaction Kinetics	b. Data Validation				Final			
	4. Thermo and Reaction Kinetics	c. Data Accuracy				Final			
	4. Thermo and Reaction Kinetics	Gasification				Final			
	4. Thermo and Reaction Kinetics	Fermentation				Final			
	4. Thermo and Reaction Kinetics	DSP				Final			
	4. Thermo and Reaction Kinetics	Other				Final			
	5. Process Structure & Description		7	9		Final			
	5. Process Structure & Description	a. Criteria and Selections				Final			
	5. Process Structure & Description	b. Process Flow Scheme (PFS).				Final			
	5. Process Structure & Description	c. Process Stream Summary				Final			
	5. Process Structure & Description	d. Utilities				Final			
	5. Process Structure & Description	e. Process Yields				Final			
	5. Process Structure & Description	Pretreatment				Final			
	5. Process Structure & Description	Gasification				Final			
	5. Process Structure & Description	Fermentation				Final			
	5. Process Structure & Description	DSP				Final			
	5. Process Structure & Description	Pumps				Final			
	5. Process Structure & Description	Posttreatment				Final			
	5. Process Structure & Description	Other				Final			
	6. Process Control		3	4		Final			
	7. Mass and Heat Balances		1	3		Final			
	7. Mass and Heat Balances	a. Practical Aspects.				Final			
	7. Mass and Heat Balances	b. Balance for Total Streams				Final			
	7. Mass and Heat Balances	c. Balance for Stream Components				Final			
	7. Mass and Heat Balances	Pretreatment				Final			
	7. Mass and Heat Balances	Gasification				Final			
	7. Mass and Heat Balances	Fermentation				Final			
	7. Mass and Heat Balances	DSP				Final			
	7. Mass and Heat Balances	Pumps				Final			
	7. Mass and Heat Balances	Posttreatment				Final			
	7. Mass and Heat Balances	Other				Final			
	7. Mass and Heat Balances	LCA				Final			
						Final			
	8. Process and Equipment Design		9	12	8	Final			
	8. Process and Equipment Design	a. Integration by Process Simulation				Final			
	8. Process and Equipment Design	b. Equipment Selection and Design				Final			
	8. Process and Equipment Design	c. Special Issues				Final			
	8. Process and Equipment Design	d. Equipment Data Sheets				Final			
	8. Process and Equipment Design	Pretreatment				Final			
	8. Process and Equipment Design	Gasification				Final			
	8. Process and Equipment Design	Fermentation				Final			
	8. Process and Equipment Design	DSP				Final			
	8. Process and Equipment Design	Pumps				Final			
	8. Process and Equipment Design	Other				Final			
	9. Wastes		3	4		Final			
	9. Wastes	a. Direct Wastes				Final			
	9. Wastes	Gasification				Final			
	9. Wastes	Fermentation				Final			
	9. Wastes	DSP				Final			
	9. Wastes	Posttreatment				Final			
	9. Wastes	Other				Final			
	10. Process Safety		3	4		Final			
	10. Process Safety	a. HAZOP				Final			
	10. Process Safety	b. FEI				Final			
	11. Economy		6	8		Final			
	11. Economy	*a. Investment (Once-off)*				Final			
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	11. Economy	*c. Annual Income*				Final			
	11. Economy	*d. Annual Cash Flow*				Final			
	11. Economy	*Economic Criteria*				Final			
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	11. Economy	*Negative Cash Flows*				Final			
	12. Creativity and Group Process Tools		2	3		Final			
	13. Conclusions and Recommendations		2	3		Final			
	14. List of Symbols					Final			
	TOTAL		51	70	8				
			target = 65 pages						
	15. Literature					Final	RT		
	Appendices				158				
1	**Appendices - General**								
1-1	Appendices - General	Feedstock choices			2	Final	DR		
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1-3	Appendices - General	Sustainability			2	Final	DR		
1-4	Appendices - General	Hydrolysis			8	Final	LF+DR		
1-5	Appendices - General	Introduction Gasification.doc			4	Final	RT+LF		
1-6	Appendices - General	Piquar process part one			1	Final			
1-7	Appendices - General	Choice of fermentation substrate.doc			1	Final	MM+RE		
1-8	Appendices - General	Mass + heat balances for ch. 7				Final	DR		
1-9	Appendices - General	DOW F&EI			2	Final	DR		
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1-11	Appendices - General	Pure component Properties			1	Final	DR		
1-12	Appendices - General	Membranes			3	Final	DR		
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1-14	Appendices - General	Aspen uitleg			7	Final	RT+DL		
1-15	Appendices - General	Air separation			3	Final	DR		
1-16	Appendices - General	Stream summary			2	Final	RT		
1-17	Appendices - General	Block scheme				Final	MM		
1-18	Appendices - General	Planning.xls Pivot table			2	Final	DL		

Document lifecycle

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2	**Appendices - Fermentation**								
2-1	Appendices - Fermentation	Stoichiometry and Kinetics			6	Final	MT + RE		
2-2	Appendices - Fermentation	Reactor types			6	Final	MT + RE		
2-3	Appendices - Fermentation	Mass + heat balances			11	Final	MT + RE		
2-4	Appendices - Fermentation	Nutrients			2	Final	MT + RE		
2-5	Appendices - Fermentation	Fermentation model MATLAB				Final	MT + RE		
06-Feb	Appendices - Fermentation	MATLAB scripts							
3	**Appendices - Gasification**								
3-1	Appendices - Gasification	Gasification kinetics.doc			4	Final	DR+DL+LF		
3-2	Appendices - Gasification	Gasificationreactors1.doc			8	Final	DR+DL+LF		
3-3	Appendices - Gasification	Fluidisation calcs.doc			6	Final	RT		
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4-2	Appendices - DSP	Downstream processing.doc			5	Final	DL+DR		
4-3	Appendices - DSP	DSP_solvent_recovery.doc			1	Final	DL		
4-4	Appendices - DSP	DSP_unit_design.doc			2	Final	DR		
4-5	Appendices - DSP	Phase equilibrium for t-butanol/water			2	Final	DL		
					1	Final	DL		
5	**Appendices - Eq. Spec. sheets**								
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5-48	Appendices - Eq. Spec. sheets	E05			1	Final	RT + DR		
5-49	Appendices - Eq. Spec. sheets	E06			1	Final	RT + DR		
6	**Appendices - Equipment summaries**								
6-1	Appendices - Equipment summaries	Reactors, columns, vessels			1	Final	DL + DR		
6-2	Appendices - Equipment summaries	Heat exchangers, furnaces			1	Final	RT + RE		
6-3	Appendices - Equipment summaries	Pumps, compressors, expanders and blowers			1	Final	DL + DR		
6-4	Appendices - Equipment summaries	Mixers & separators			1	Final	DL + DR		
6-5	Appendices - Equipment summaries	Miscellaneous			1	Final	DL + DR		
7	**Appendices - Capital cost sheets**								
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7-2	Appendices - Capital cost sheets	Utility requirements				Final	LF		
7-3	Appendices - Capital cost sheets	Product costs per unit				Final	LF		
7-4	Appendices - Capital cost sheets	Raw material cost per unit				Final	LF		
7-5	Appendices - Capital cost sheets	Capital costs - Reactors and columns				Final	LF		
7-6	Appendices - Capital cost sheets	Capital costs - Compressors and expanders				Final	LF		
7-7	Appendices - Capital cost sheets	Capital costs - Heat exchangers				Final	LF		
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7-9	Appendices - Capital cost sheets	Capital costs - Miscellaneous				Final	LF		
7-10	Appendices - Capital cost sheets	Cumulative cash flows				Final	LF		
7-11	Appendices - Capital cost sheets	Sensitivity analysis				Final	LF		
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8-6	Appendices - Visits to experts	Visit to Moulijn - gasification			1	Final	DL + RE		
8-7	Appendices - Visits to experts	Visit to Particle technology			1	Final	RT + LF		

Appendix 1-19: Life cycle of the product and crucial elements

Poly-ß-hydroxybutyrate (PHB) is polymer produced by living organisms. It is an energy storage product of microorganisms that is produced during nutrient scarce situations. PHB is considered a substitute for many, non-biodegradable (conventional) polymers that nowadays exist. Conventional polymers are produced from fossil fuels and after being consumed, conventional polymers are recycled, dumped or combusted. Another point of the conventional polymers is that, since they are produced from fossil fuels they contribute to the global warming. Besides this, conventional polymers don't degrade in a natural environment (degradation takes very long time). This last aspect is the main reason why the production of biodegradable polymers is so attractive. A variety of applications arise thanks to this property of PHB: agricultural utilities, speciality products (alpinism articles), etc.

Because PHB is a natural product and because HB (hydroxybutyrate) a natural constituent of blood is, interesting medical applications arise.

The life cycle of a product

Depending on the application of the PHB it will follow one or another life cycle path, which can be separated in three stages:

- Production of the raw materials an product
- Consumption (application)
- Waste management and degradation.

All tree stages are interrelated with each other. For example:

- The production of a product is dependent of the application of it.
- Depending on the application degradation or waste management follows one path or another.

The first stage (Production)

Different options are available for the first stage but there are some things that all the options have in common: the PHB is produced by fermentation of an organic substrate. There exists one option that is not permitted in the Netherlands: using transgenic plants for PHB production.

Until now all the existent PHB production processes start from plants or crops. From these raw materials, sugars are get whose are fermented into PHB. Then PHB is separated with DSP techniques, which utilize environmentally unfriendly solvents and materials.

The designed process uses wood as feedstock (raw material). Wood is produced when plants fixate carbon dioxide from air and nutrients from soil and water. Once wood is cutted from the trees it is transported to the PHB production plant, where it is gasified and converted through fermentation into PHB. The DSP uses less solvents and substances than that of the existent processes. The designed process produces almost no wastes, see chapter WASTES.

The process seems thermodynamically illogic since first sugars (raw material) are break down into syn-gas (simple molecules) and then again build up into biomass. This is something that happens continuously in the crude oil industry, for example for the production of methanol. The question why this is usually done is because the raw material poses such a complexity that selection of the appropriate part for one application is not easy.

Second stage (consumption)

Once PHB is produced it is transported to the manufacturer that utilises it for the production of a specific consumer product. From there it is distributed in the consumers market, sold and consumed.

Third stage (Waste management & degradation)

After being consumed the PHB, its elements enter then again in the global material cycles; excepting when PHB is recycled. After consumption (coffin, agricultural application, food packaging, etc) PHB is degraded by microbial attack and decomposed into CO_2, biomass, H_2O etc. Thus finally the decomposition products arrive into the different environmental compartments (air, soil, water).

When PHB is recycled it finally also arrives into the natural material cycle, but it takes more time. It is common that people think that recycling is always the most environmental friendly option. In the case of PHB is recycling not the best option because to recycle the PHB (what is produced with the effort of the sun that is free and inexhaustible) huge amounts of transport fuels and logistic effort is required. But in the case PHB is not recycled the effort of decomposing and bring back the elements and nutrients back to nature is done by nature itself. Besides that if PHB is recycled (to turn it back to the monomer or melt it) it could not be mixed with other plastics, this makes indispensable a total new collecting system.

Environmental issues

Energy

In environmental discussions, one of the most important questions is how much energy is necessary over the entire life cycle. An interesting point is that most of the energy input (for biomass, PHB production-consumption and degradation) comes from the sun. Of course the energy saved in non-renewable sources (Crude Oil, carbon etc) comes also from the sun, but over a very large time span. In the case of biomass and thus the produced PHB, the energy is saved over a relatively short time span, and therefore it doesn't produce accumulation of carbon dioxide in the environment since all de fixed carbon is coming from CO_2 and it will be again fixed.

Nutrients

Another important aspect is the conservation of nutrients. When wood is gasified many nutrients that compose the biomass (wood biomass) attached to proteins, enzymes, coenzymes, etc are oxidised to a less attractive form for example: organic nitrogen is turned into molecular nitrogen. The process (microbial process) that turns this again into a more attractive form is a very slow process. The same situation holds for phosphor and sulphur compounds. This leads to a negative accumulation of the more accessible form of nutrients.

The next figure represents the material flows between the different environmental compartments and the PHB production-consumption chain.

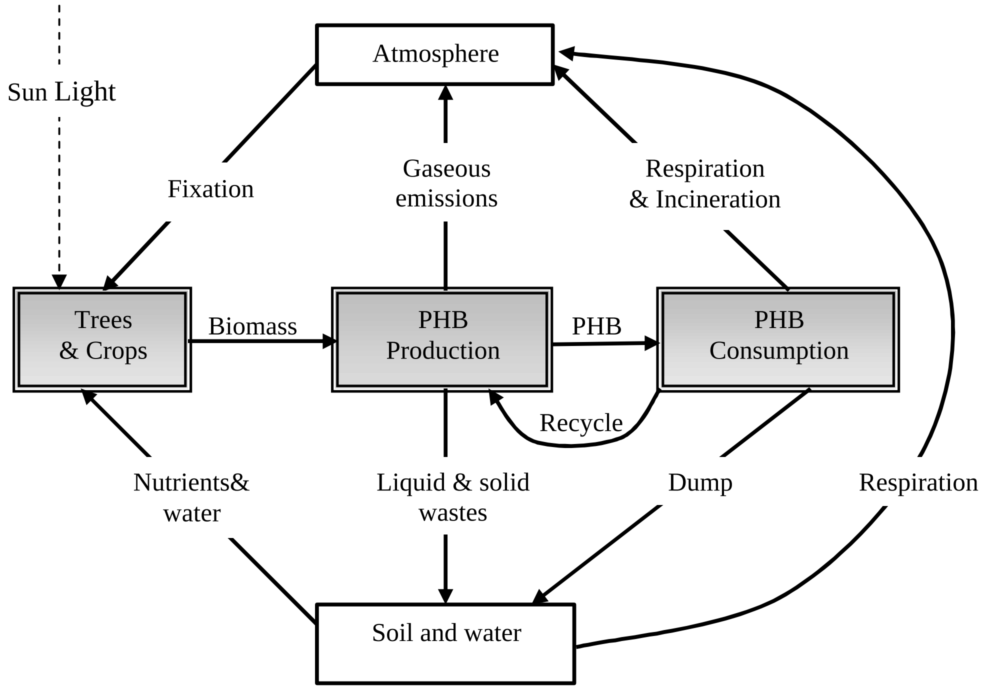
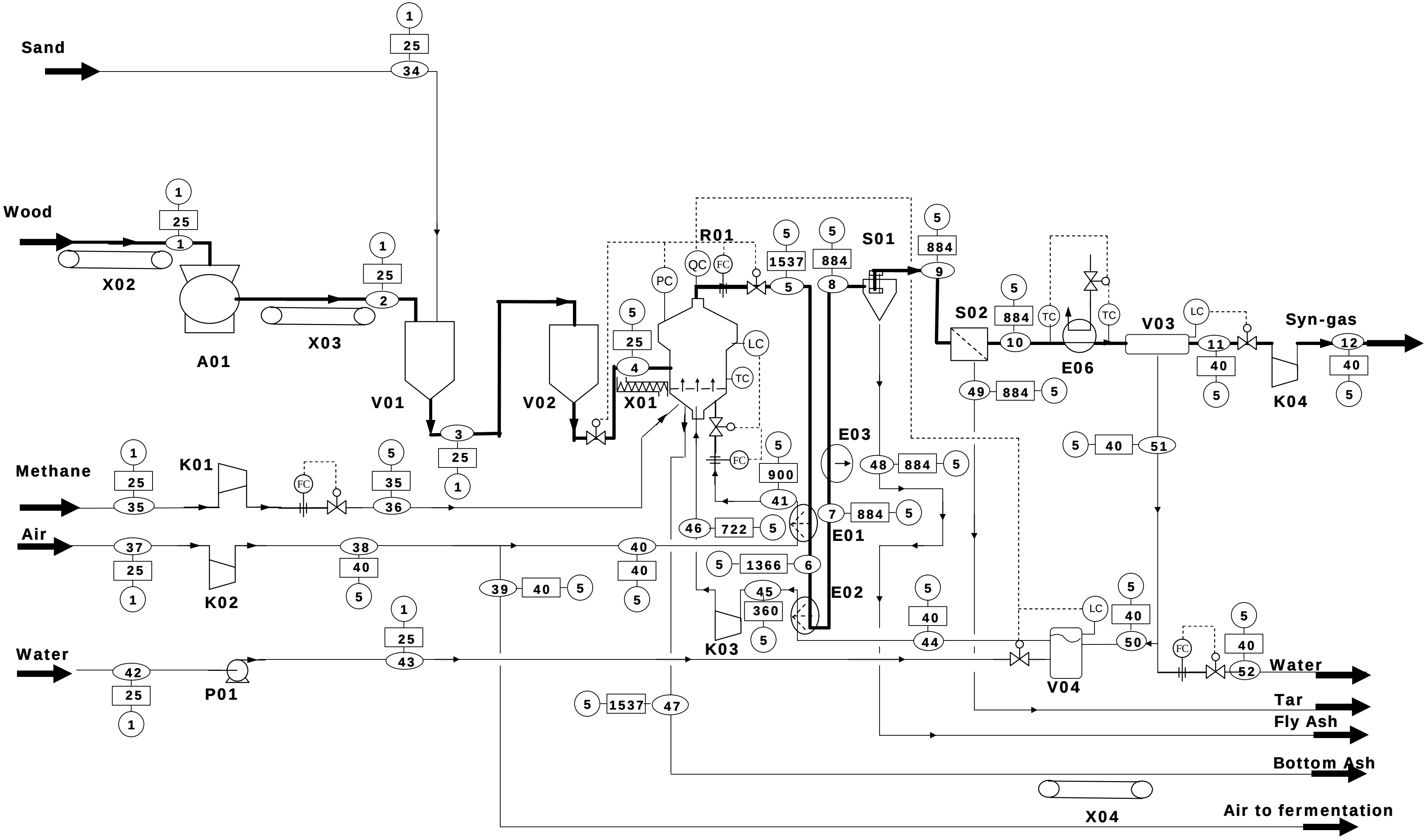
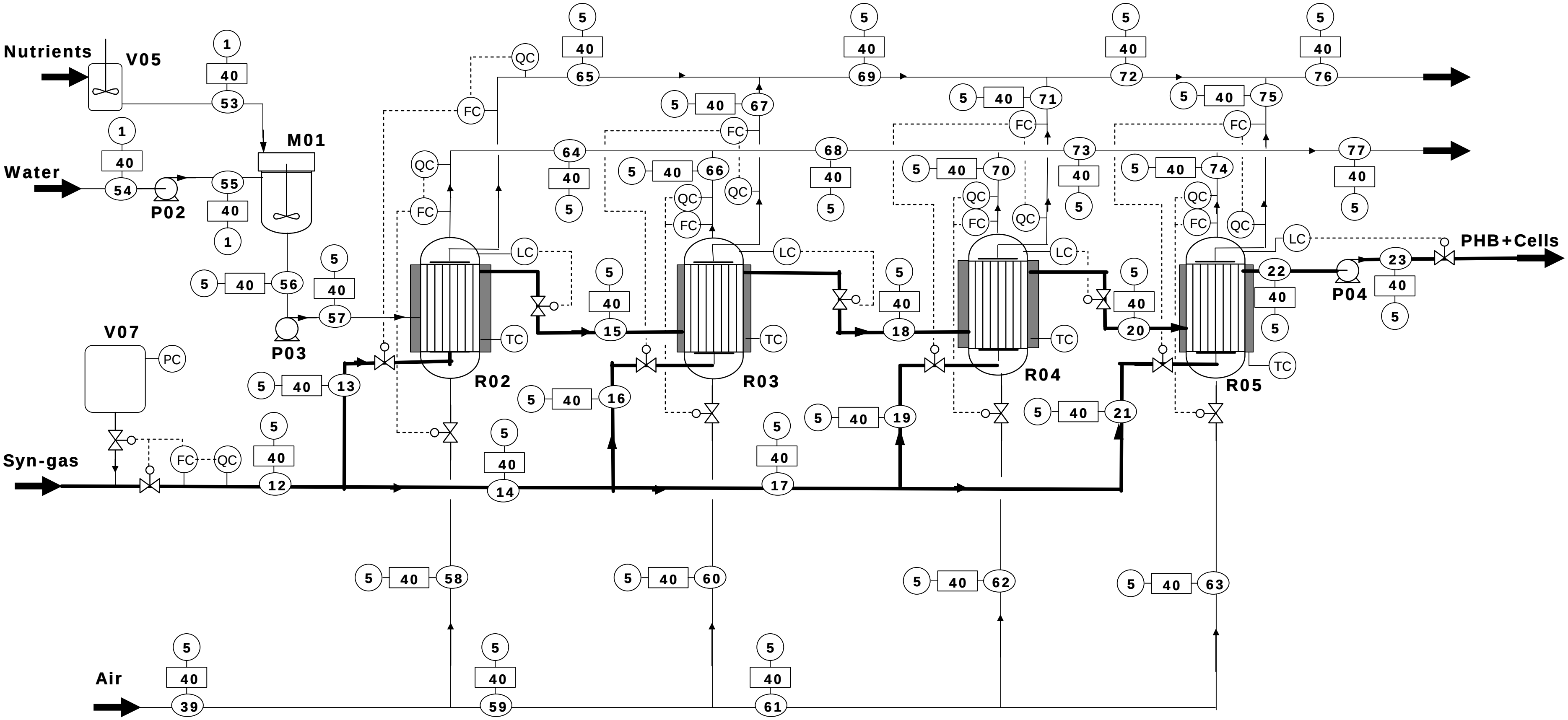


Figure 1: Material flows (carbon, hydrogen, oxygen, nutrients). The two with blocs represent the environmental compartments and the grey blocs represent the PHB production-consumption chain. The arrows represent the material flows between the different compartments.

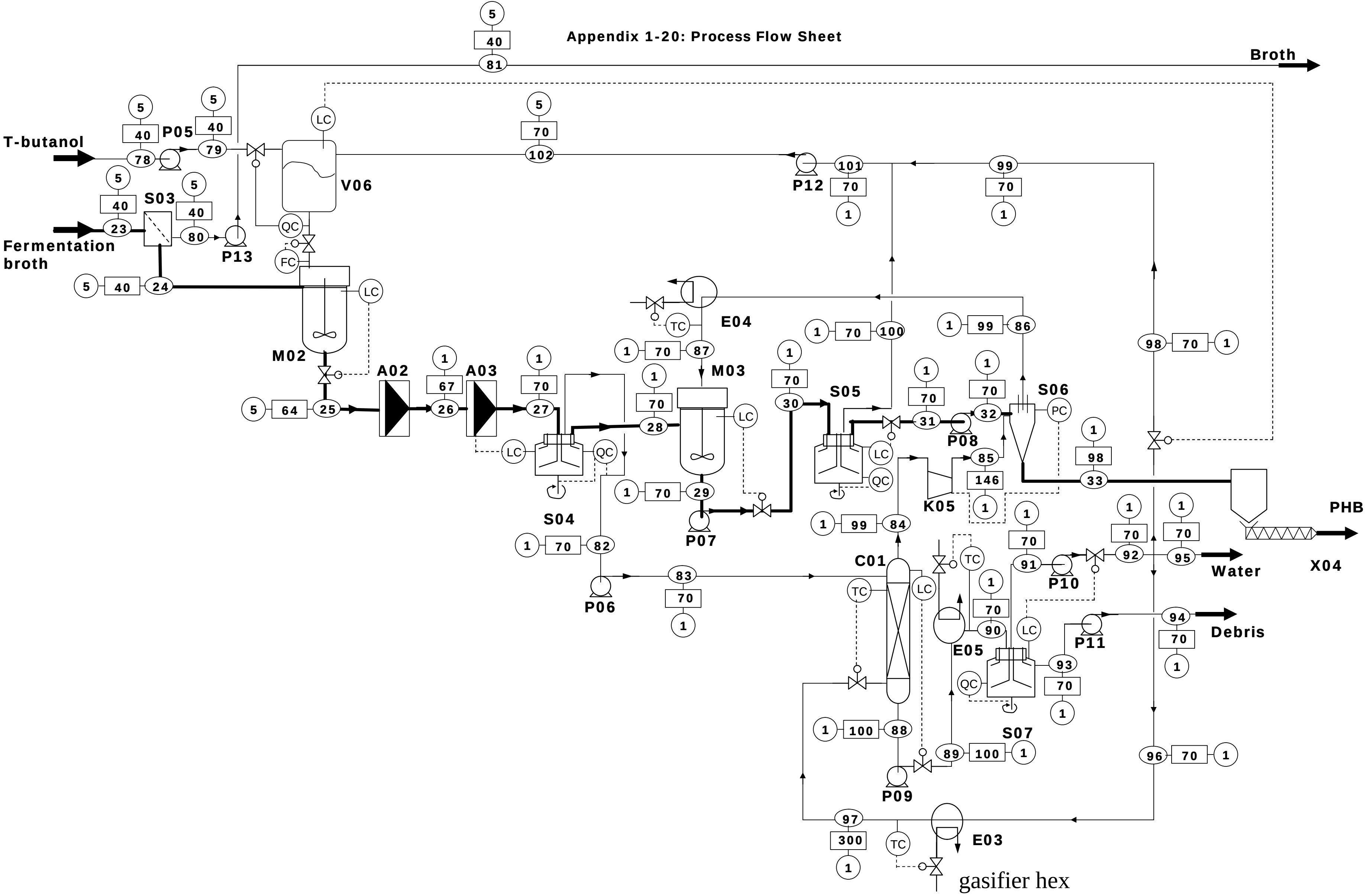
Appendix 1-20: Process Flow Sheet



Appendix 1-20: Process Flow Sheet



Appendix 1-20: Process Flow Sheet



Appendix 2:
Fermentation

2-1 Stoichiometry

For the calculations of the requirements (H_2, CO, O_2) for the PHB production some assumptions where made because of the lack of information concerning syn-gas fermentations. It is demonstrated that syn-gas can be aerobically fermented [Marshall 1998]. But information concerning stoichiometry of the micro-organisms that is capable of consuming H_2 and CO simultaneously is not published.
The assumptions made are the following:

- For the kinetic parameters (growth rate) it is assumed that they are equal to those of the Alcaligenes eutrophus.
- The same amount of energy is produced when carbon monoxide is oxidised as when hydrogen is oxidised. That means the same energy equivalents are produced. [Schlegel 1987]
- It is assumed that the micro-organism growth with the same stoichiometry.

The assumptions were supported by literature since the micro-organisms capable of fermenting synthesis gas and Alcaligenes eutrophus are very related to each other. Also the consult of an expert supported the assumptions made.

2.1.1 Stoichiometry of growth and PHB production

In order to calculate the required amount of substrate needed for microbial biomass production in the "growth reactor" and the amount of substrate needed for PHB production stoichiometry relations are necessary. The stoichiometry of growth for hydrogen fermenting bacteria is the following [Schlegel 1987]:

$$6\,H_2 + 2\,O_2 + CO_2 \rightarrow \,<CH_2O> + 5\,H_2O$$

In which $<CH_2O>$ represents the microbial biomass. Carbon monoxide fermenting bacteria are closely related to hydrogen fermenting bacteria and syn-gas fermenting bacteria [Schlegel 1987]. All carbon monoxide fermenting bacteria can ferment hydrogen as well [Schlegel 1987]. However little is known about carbon monoxide utilising bacteria. For this reason data concerning growth and PHB production is used of the hydrogen fermenting bacteria Euthropus Alcaligenes. For calculations it is assumed that this bacteria can also ferment carbon monoxide. Carbon monoxide is used to supply energy by the reaction:

$$CO + \frac{1}{2}\,O_2 \rightarrow CO_2$$

This reaction supplies approximately the same amount of energy as when hydrogen is oxidised [Schlegel 1987]. As a consequence it will be assumed that every hydrogen molecule used in the catabolism can be replaced by a carbon monoxide molecule. Stoichiometrically only one hydrogen molecule is fixed in the biomass during the anabolism. The formed carbon dioxide molecule from the above reaction is subsequently used as a C-source. Thus the net growth reaction on synthesis gas will be:

$$x\,H_2 + 2\,O_2 + (6\text{-}x)CO \rightarrow \,<CH_2O> + (x-1)\,H_2O + (5\text{-}x)\,CO_2$$

In which *x* ranges from 1 till 6, since 1 hydrogen molecule needs to be fixated into the biomass. Note that if x is larger than 5, carbon dioxide will hardly be consumed.
In practice the bacteria will utilise all the carbon dioxide and hydrogen transferred to the liquid phase, since mass transfer is the limiting step. In order to use the correct stoichiometry the ratio of transferred hydrogen and carbon monoxide is defined:

$$TR_{H_2/CO} = \frac{\text{moles of hydrogen transferred}}{\text{moles of carbon monoxide transferred}}$$

In which $TR_{H2/CO}$ stands for the transfer ratio. This ratio has to equal the ratio of hydrogen and carbon monoxide in the growth relation, since all the substrate is consumed. Thus combining the latter equation with the net growth relation gives the growth relation for a certain transfer ratio of hydrogen and carbon monoxide:

$$\frac{6\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}H_2 + 2O_2 + \frac{6}{1+TR_{H_2/CO}}CO \rightarrow <CH_2O> + \frac{5\cdot TR_{H_2/CO}-1}{1+TR_{H_2/CO}}H_2O + \frac{5\text{-}TR_{H_2/CO}}{1+TR_{H_2/CO}}CO_2$$

In which the ratio can vary from 0.2 till infinity, since one hydrogen molecule has to be fixed into the biomass.

The stoichiometry reaction for the PHB for hydrogen fermenting bacteria production is as follows [Schlegel 1961]:

$$25\ H_2 + 8\ O_2 + 4\ CO_2 \rightarrow \text{-}\left[C_4H_6O_2\right]\text{-} + 22\ H_2O$$

In which $–[C_4H_6O_2]$- is the dehydrolysed monomer of PHB. This reaction can also be converted to a net reaction with carbon monoxide giving:

$$x\ H_2 + 8\ O_2 + (25\text{-}x)\ CO \rightarrow \text{-}\left[C_4H_6O_2\right]\text{-} + (x\text{-}3)\ H_2O + (21\text{-}x)\ CO_2$$

x ranges from 3 till 25, since 3 hydrogen molecules need to be fixated into the PHB. Note that if *x* is larger than 21, carbon dioxide will be net consumed.
Following the same reasoning as for the growth stoichiometry, the stoichiometry for PHB production at a certain transfer ratio will be;

$$\frac{25\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}H_2 + 8O_2 + \frac{25}{1+TR_{H_2/CO}}CO \rightarrow -\left[C_4H_6O_2\right]- + \frac{22\cdot TR_{H_2/CO}-3}{1+TR_{H_2/CO}}H_2O + \frac{21\text{-}4\cdot TR_{H_2/CO}}{1+TR_{H_2/CO}}CO_2$$

In which the ratio can vary from 0.14 till infinity, since three hydrogen molecules have to be fixed into the PHB.

From the soichiometry the yields on substrate follow. Yield is defined as follows:

$$Y_{ij} = \frac{?i}{?j} = \frac{\text{Amount of j produced}}{\text{Amount of substrate i used}}$$

For a given amount of hydrogen and carbon monoxide transferred one can calculate the amount of biomass or PHB produced.

2-2 Reactor types

The reactor type has to be chosen carefully because of two main reasons. First of all, the explosion danger because of the presence of hydrogen and oxygen poses a serious safety threat. Hydrogen becomes explosive for mixtures air hydrogen at 1 bar: 81.8% air and 18.2% hydrogen, and for pure oxygen-hydrogen mixtures at 1 bar: 85% oxygen and 15% hydrogen.

The second reason for a carefully election is because of the limitation of the mass transfer, due to the fact that gases such as hydrogen, oxygen and carbon monoxide dissolve poorly in water.

Moreover considerations as maximisation of the conversion of the feedstock and reduction of the total costs of the reactor play also an important role.

After delivering the possible reactor alternatives the group has chosen a number of alternatives suitable for a safe and effective operation:

- Bubble column
- Membrane bioreactor
- Monolith reactor
- Tray reactor

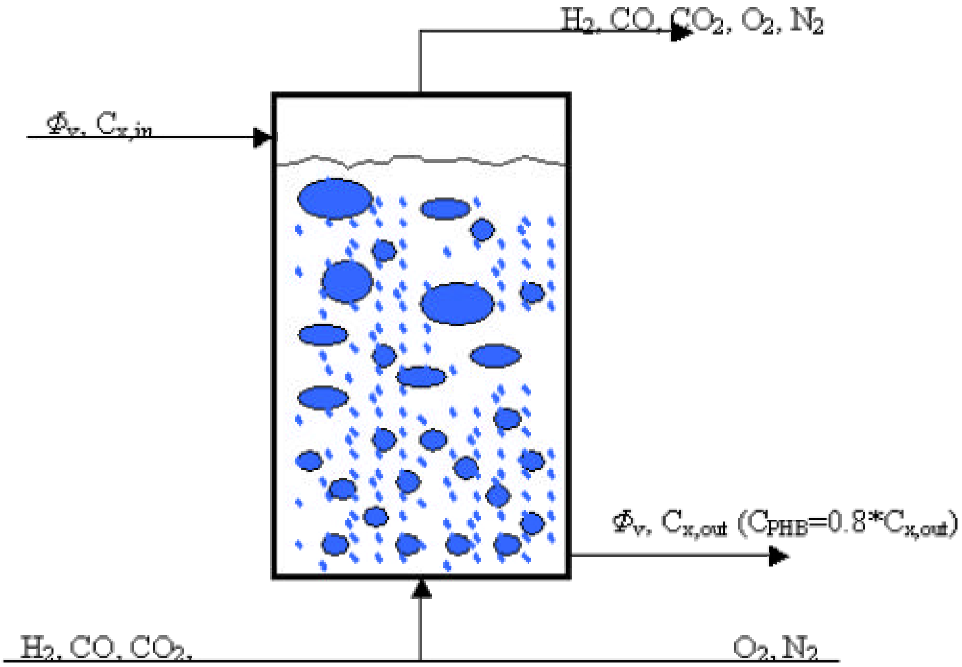


Figure 1:Bubble reactor for syn-gas fermentation

2.2.1 The bubble column

The bubble column is the most common reactor type in biological processes where a gaseous phase is present. The main advantages of this reactor are the low investment and operating costs and a simple mechanical construction, besides this type of reactors are well mixed. [Moulijn 2001]
General disadvantages of this type of reactors are the difficulty to scale up and the loss of effective contacting area when the reactor is bigger than 30 m3 due to bubbles coalescence. To avoid this last problem bubble columns require highly effective spargers to crate as small as possible bubbles.
More specific disadvantages of this reactor type is the higher explosion danger. Syn-gas and oxygen (air) are blown into the reactor together. To avoid this problem two solutions exist:

- Operate at very low gas concentrations. Concentration of hydrogen in the gas phase (input) must be lower than 18 vol-% [Chemiekaarten 2003]. When syn-gas is produced autothermically and nitrogen is present the volume fraction of hydrogen gas is generally lower than 20 vol-%. This would lead to a considerably larger reactor due to mass transfer limitations, since hydrogen and carbon monoxide dissolve poorly in water.

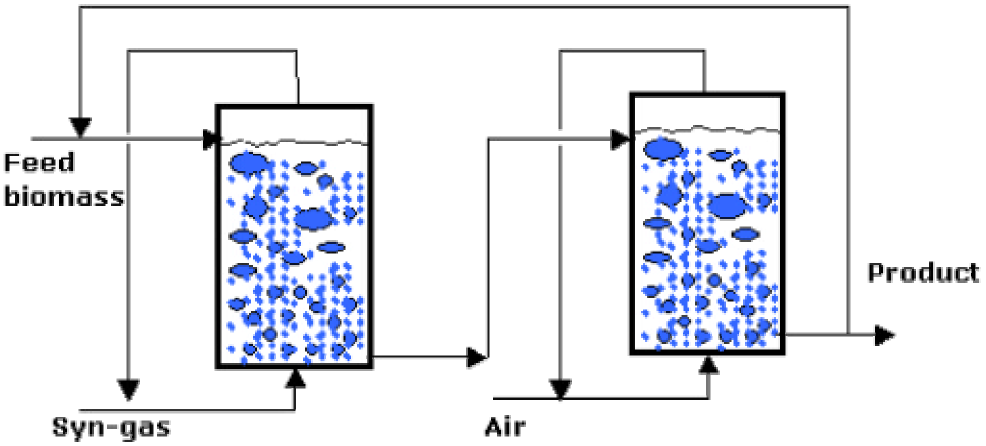


Figure 2:Two bubble columns in series. One for syn-gas feeding and one for oxygen feeding

- Operate two bubble columns in series, one for feeding the carbon and energy source (CO, CO_2 and H_2) and one for aeration. This system becomes interesting when syn-gas is free of nitrogen (that means allothermic gasification), since mass transfer can be facilitated due to higher concentrations in the gas phase. This would lead to the construction of two reactors for the production of PHB.

Advantages of this configuration are the reduced explosion limits and the high syn-gas conversion; feeding the gases separately makes recycle of unreacted gases possible. Additionally, it is very expensive to recycle gases. Disadvantages of this configuration are the expected lower production velocity and consequently the relative larger reactor dimensions ($V_{r1}+V_{r2} > V_{single}$). But since the single configuration has to be operated at lower gas concentrations this statement may not necessarily be true.

2.2.2 Membrane bio-reactor

A novel bio-reactor is the membrane bio-reactor. In this type of reactor membranes are used for gas transfer. The advantage of using membranes over bubbles is the possibility to separate the two gas phases: hydrogen rich syn-gas and oxygen source; and the constant contacting area of the membranes. One disadvantage is the growth of a biomass film on the membranes and the higher investment and operation costs of the reactor. Operation costs are caused by the higher pump costs and regular maintenance of the membranes.
For a good mixing of the reactor liquid, recycle of the outlet stream could be reasonable. One solution to the biomass film is sufficient mixing. This can be achieved by sparging air or oxygen trough the liquid phase, this would also reduce investment costs because of less membrane units will be required.

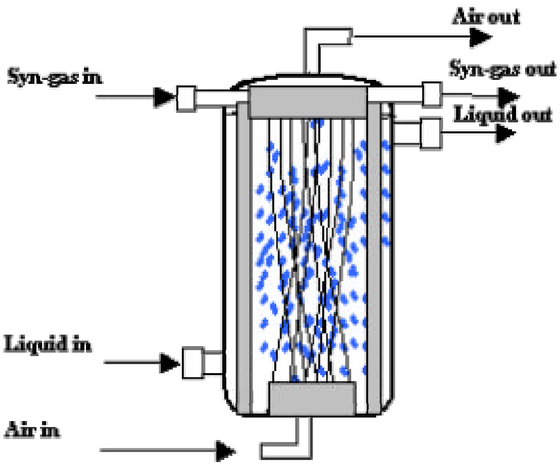


Figure 3:Membrane (bio)reactor. Hydrogen supplied trough membranes and air by bubbles

The volume of the reactor can be reduced considerably, compared to the bubble column, because increasing the number and packing density of the membranes the contacting area can be increased. A positive consequence of this is the higher achievable product concentrations and consequently the lower down stream processing costs.
Since syn-gas is directly consumed, stripping by the gas bubbles of hydrogen and carbon sources (CO and CO_2) is almost eliminated, which facilitates higher conversions and reduce explosion risk compared to the single bubble column configuration.

The membranes require regular cleaning due to fouling. To avoid stopping the continuous process membrane units can be cleaned one by one replacing the fouled one with a clean membrane unit.

2.2.3 Monolith bio-reactor

Monolith reactors are known because of their high mass transfer capacity, something that makes this reactor very attractive for this process. The high contacting area between the gas phase and the liquid phase is responsible for this property. The lower pressure drop of monolith reactors means lower pump costs (this doesn't mean lower investment costs). It is evident that the investment costs of this reactor are considerably higher to those of the bubble column and possible also to those of the membrane bio-reactor.

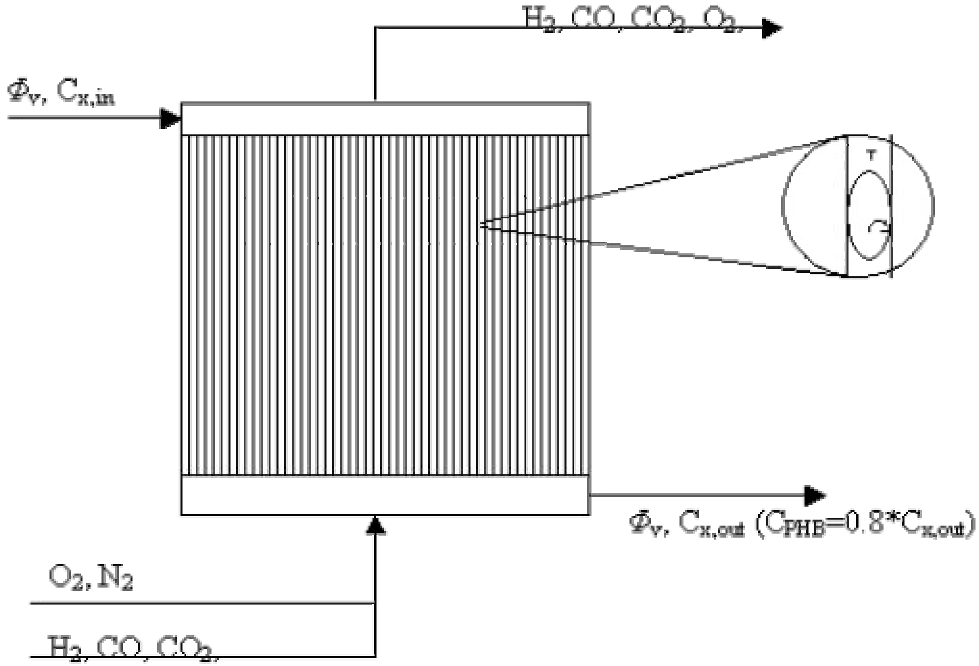


Figure 4:: Monolith bio-reactor for the production of PHB.

The higher mass transfer capacity can lead to lower reactor volumes and higher conversions. However the explosion risk can only be avoided as in the case of the bubble reactor: low gas phase concentrations or reactors in series (stages). The, expected high investment cost of the series reactors rejects this solution.

2.2.4 Tray reactor

In biological processes tray reactors are mainly used for packed biomass or enzymes. This reactor type is not available on the market. The major advance of this system is the low explosion danger in combination with the high syn-gas conversion. To achieve high mass transfer a high number of trays would be necessary, which would increase investment costs. More disadvantages are the maintenance costs since fouling of the trays is unavoidable (due to low mixing) and difficult operability.

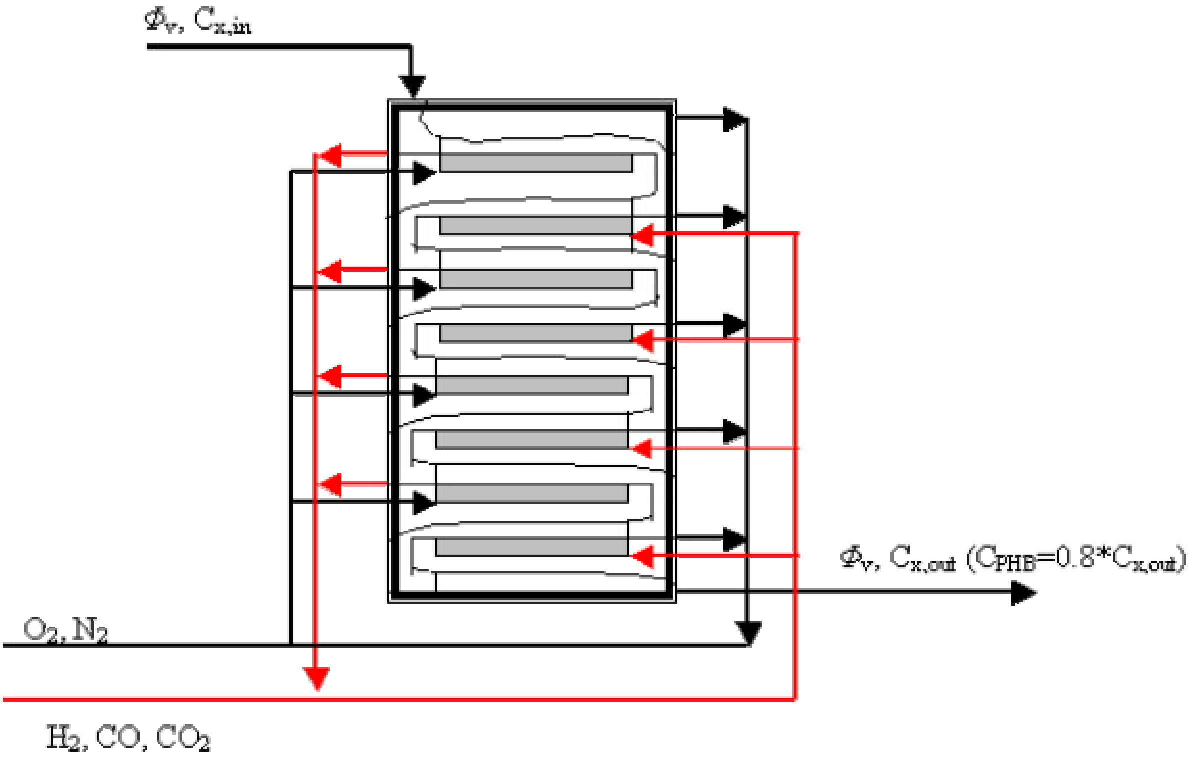


Figure 5:: Tray reactor with recycle of the unreacted gases.

The low explosion risk and the high syn-gas conversion are achieved by feeding the two hazardous gases (hydrogen and oxygen) separately. This makes this reactor suitable for the process under consideration. Nevertheless the expected investment costs, the uncertainty of the design and the operability considerations lead to reject of this option.

2.2.5 Continuous stirred reactor with micro-bubbles.

The continuous stirred tank reactor with micro-bubbles is well studied for syn-gas fermentations for PHB productions [Heijnen 2003]. It is possible to operate it with safe gas mixtures and achieve reasonable mass transfer. One disadvantage is the large energy requirement for the micro-bubble sparger and stirrer.

2.2.5 Continuous stirred reactor with micro-bubbles.

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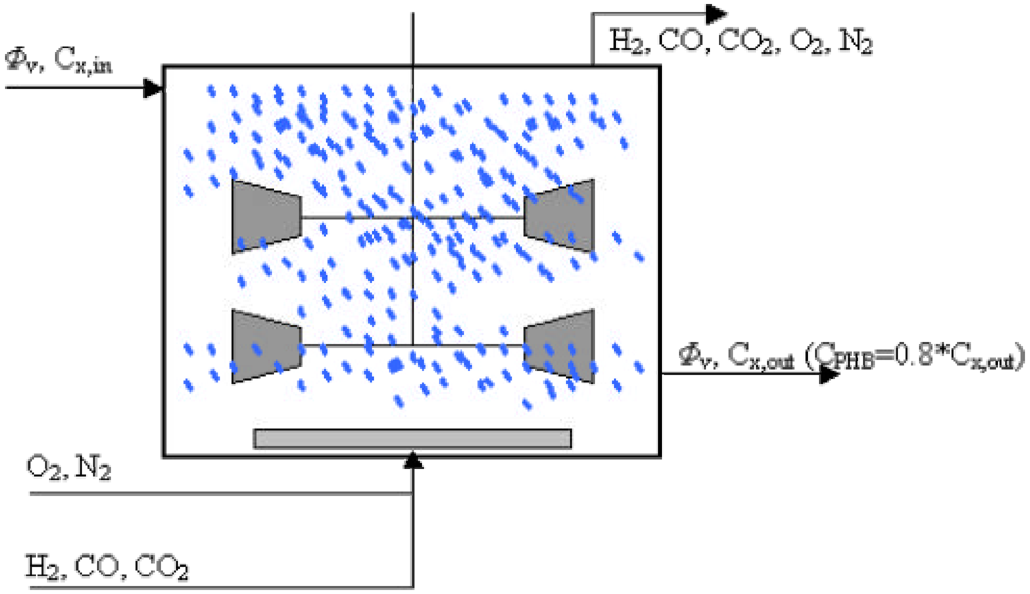


Figure 6: CSTR with micro-bubbles. Lower explosion limits and high mass transfer.

This reactor seems to be suitable for this process; hence it is considered in weighing the advantages and disadvantages of each of the proposed reactors for an effective selection. After having considered the 5 reactor types 3 of them seem to be the true competitors: The bubble column (single or series), the membrane bioreactor and the CSTR with micro-bubbles.

2-3 Mass and heat balances for the calculation of the dimensions of the reactor

For the dimensioning of the reactor many things are crucial. First it has to be defined if the process will run continuously or batch wise. Secondly the configuration of the reactor, whether the syn-gas or air is going to flow through the membranes, etc. And finally the mass and energy balances have to be drawn.

2.3.1 Continuous vs. batch production

The Fermentation sub-process consists of the microbial biomass growth phase and a PHB accumulation phase. In a batch process both phases will take place in the same reactor, while in a continuous process the growth and production phase will take place in separate reactors. In order to decide between continuous and batch operation first some advantages and disadvantages of both methods will be discussed.

For operability reasons continuous processes are usually used in processes with a production capacity greater than 5000 tons/yr, whilst a process with a capacity less then 500 tons/yr is usually a batch operation [Douglas 1988]. Plants with capacities in between both extremes have to decide between continuous or batch based on specific product or process properties, as is the case for the process described in this report.

In most cases continuous reactors have a smaller residence time and consequently a smaller reactor volume compared to batch reactors. Continuous reactors also have a smaller down time, since they only go down once a year for maintenance and cleaning operation. In this special case where syn-gas is fermented no storage of the syn-gas is necessary for continuous operation. The gas can be continuously fed to the growth and production reactors. Therefore the DSP (down stream process) is also continuous, this implies no storage facilities for the produced PHB.

In bioprocesses the main advantage of batch plant is the fact that the whole batch can be sterilised in the batch reactor (pre-heating of the substrates and solvent before the batch starts), whilst for a continuous reactor all separate substrate and solvent streams have to be sterilised separately. In practice this makes continuous operation of bioprocesses more expensive. In syn-gas fermentation however contamination is very unlikely to occur due to the fact that the substrate is highly toxic to almost all living organisms; consequently sterilisation is not necessary. A further advantage of batch operation is that some cleaning operations, which should be done regularly, can be done at the end of a batch. Membranes used in a bioprocess for example require regular cleaning because of biomass film formation on the membranes. These maintenance problems can however also be overcome in a continuous reactor. There is another reason to choose for a batch reactor concerning its flexibility. Several products can be produced in a single reactor. However the design of this process is not directed to a multipurpose plant.

For this process there is chosen for continuous operation, mainly due to the fact that storage of syn-gas and the produced microbial biomass is unnecessary. At first estimate continuous operation should give the better results in terms of costs.

Process block diagram

When a cell is producing PHB it does not grow. This is because nutrients required for the production of the building blocks of biomass are not available. That means that for a continuous process the biomass (microbes) have to be produced in a different reactor than where the PHB is produced. Therefore two separate and interconnected reactor units have to be designed. The next figure give a process block diagram of the fermentation section of the PHB production process, composed by a section for the growth of microorganisms and a section for the production of PHB.

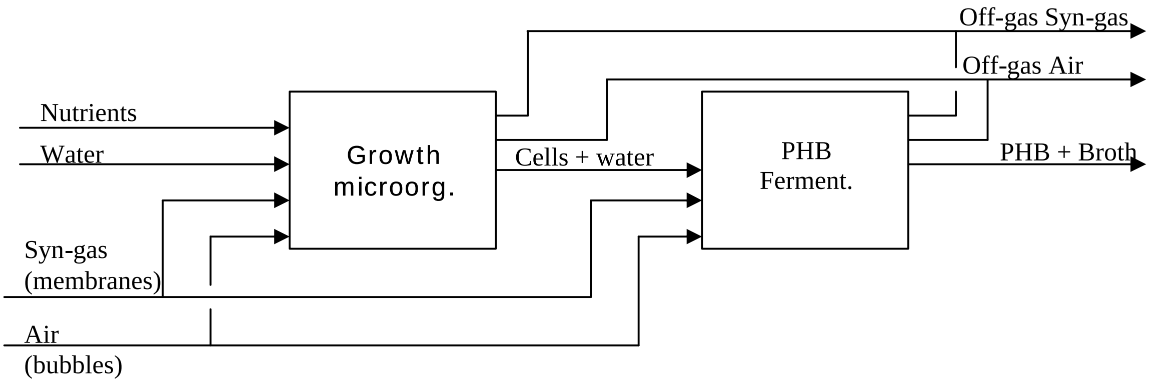


Figure 1: Block diagram of the syn-gas fermentation for the production of PHB

2.3.2 Balances

Microbial biomass

For the calculation of the dimensions of the reactor mass balances and energy balances have to be derived. The substrate for the fermentation is mainly constituted of gases (H_2, O_2, CO, etc.). Since micro-organisms can only grow in hydrated media, the substrate has to be transferred from the gas phase into the liquid phase. In most of the microbial fermentations where gases have to be transferred into liquids the reactions (growth and product formation) are mass transfer limited. Through the mass balances of biomass several parameters and variables are already set. The data acquired from these balances is coupled to the mass transfer balances in order to give all data for the design. Only microbial biomass concentration parameter could be chosen coming from the growth reactor. Therefore the total biomass (biomass + PHB concentration) concentration coming from the production reactor will be 200 kg/m^3. Concentration around 200 kg/m^3 are common in industry and prof. J.J. Heinen confirmed that this concentration should be possible [Suzuki, 1986].

PHB mass balance

From the PHB balance over the production reactor the flow rate follows:

$$0 = f_v \cdot C_{PHB,in} - f_v \cdot C_{PHB,uit} + production\_PHB$$

$$f_v = \frac{production\_PHB}{C_{PHB,uit}}$$

Since the PHB concentration is fixed because of the chosen microbial biomass concentration and the production of PHB is also known, the liquid flow rate is also fixed and thus known.

In the growth reactor the microbial biomass should be produced for the PHB production in the production reactor (microbial biomass acts like a catalyst). Since there’s no accumulation between the two reactors the outgoing flow rate has to be equal to the flow rate going to and coming from the production reactor. The biomass concentration is the outgoing flow has to be equal to the residual biomass (microbial biomass) concentration in the production reactor. Therefore the biomass balance in the growth reactor follows:

$$\frac{dV\cdot C_x}{dt}=0=f_V\cdot C_{x,in}-f\cdot C_x+V_L\cdot m\cdot C_x$$

Since the ingoing biomass concentration equals zero the balance reduces to:

$$0=C_x\left(m-D\right)$$

$$where$$

$$D=\frac{f_v}{V_l}$$

From this equation it follows that μ equals D. The maximal growth rate for alcaligenes eutrophus, growing on syn-gas, equals 0.21 h^{-1} [Heinzle, 1980]. To minimise reactor volume the growth and product formation of the bacteria (alcaligenes eutrophus) has to be maximal. Since the process is mass transfer limited, the reactor has to be optimised to maximise the gas to liquid transfer.
The required mass transfer rates follow from the stoichiometric balance for biomass growth. This balance is dependent on the ratio of hydrogen over carbon monoxide [see appendix 2-1]. From the stoichiometric balance the yield of biomass on the different substrates can be determined.

Because of the mass transfer limitations the reactors have to be designed according to this parameter. Therefore the rate of growth and PHB production are linearly related to the mass transfer rate. To calculate the mass transfer (amount of hydrogen, carbon monoxide-dioxide and oxygen to be transferred) necessary for the growth and PHB production mass balances over the gas phase have to be derived.
The mass transfer requirements are calculated according to the limiting reactant as follows:

$$f_{m,PHB,out}=f_{m,prod,PHB}\cdot f$$

$$J_{\text{limiting reactant}}\cdot A_{\text{interface}}=\frac{1}{Y_{\frac{\text{limiting reactant}}{PHB}}}f_{m,PHB,out}$$

The assumption that hydrogen is the limiting reactant is based on the fact that its solubility in water is very poor, the concentration in the gas phase is low and the stoichiometric requirements of this substance are the highest.

Mass balances for gas transfer over the membrane
For the membrane bioreactor two possibilities exist:

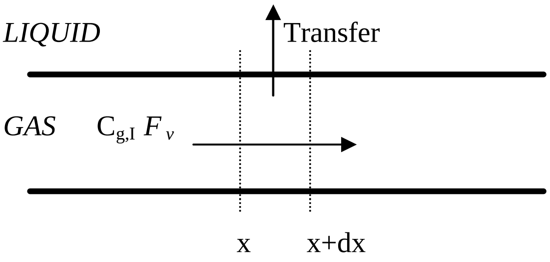
Open-end membranes.
Sealed-end membranes

After consulting an expert [Van der Lans] over the advantages and disadvantages of this two types of membrane units, it was concluded that it is better and more efficient to use open-end membranes. The main disadvantage of the sealed-end membranes is that the membranes are not efficiently utilised since (the sealed-end) mass transfer is very reduced or almost non-existent.

Appendix 2-3: Mass and heat balances for the calculation of the dimensions of the reactor

As mentioned in the appendix over reactor types [see appendix 2-2] the main advantage of the membrane bioreactor is the possibility to feed the gases into the reactor separately, avoiding or reducing explosion risks. Another interesting feature is the possibility to choose the contacting area between gas and liquid.

The mass balances are similar to those of the bubble column with difference that no pressure drop exists over the length over the membranes (pressure drop is negligible).



Mass balance per component (i) over the gas phase

$$0 = \text{in}_i - \text{out}_i - \text{transfer}_i$$

$$0 = f_v C_{g,i}\big|_x - f_v C_{g,i}\big|_{x+dx} - k \cdot (C^*_{g,i} - C_{l,i}) \cdot n \cdot \Delta A_{membr}$$

$$C_l \approx 0 \quad \text{For the limiting reactants } (H_2 \text{ or } CO)$$

$$\frac{d(f_v C_{g,i})}{dx} = -p \cdot D_{membr} \cdot n \cdot k \left(\frac{C_{g,i}}{m_i} - C_{l,i} \right)$$

$$C_{g,i} \frac{df_v}{dx} + f_v \frac{dC_{g,i}}{dx} = -p \cdot D_{membr} \cdot n \cdot k \left(\frac{C_{g,i}}{m_i} - C_{l,i} \right)$$

$$\frac{dC_{g,i}}{dx} = \frac{-p \cdot D_{membr} \cdot n \cdot k \left(\frac{C_{g,i}}{m_i} - C_{l,i} \right) - C_{g,i} \frac{df_v}{dx}}{f_v}$$

Total Mass balance over the gas phase

$$0 = \text{in} - \text{out} - \text{transfer}$$

$$0 = f_{mol}\Big|_{x} - f_{mol}\Big|_{x+dx} - \sum k \cdot (C^{*}_{g,i} - C_{l.i}) \cdot n \cdot \Delta A_{membr}$$

$C_l \approx 0$ For the limiting reactant (H_2 or CO)

$$\frac{df_{mol}}{dx} = p \cdot D_{membr} \cdot n \sum k \left(\frac{C_{g,i}}{m_i \cdot Mn_i} - C_{l,i} \right)$$

$$\frac{df_{mol}}{dx} = \frac{d\left(\frac{f_v P}{RT}\right)}{dx} = \frac{P}{RT}\frac{d(f_v)}{dx} =$$

$$\frac{df_v}{dx} = -\frac{p \cdot D_{membr} \cdot R \cdot T \cdot n}{P} \sum k \left(\frac{C_{g,i}}{m_i \cdot Mn_i} - C_{l,i} \right)$$

The mass transfer coefficient can be calculated as follows:

For the liquid phase :

$$k_l = sh \frac{Diff}{D_{membr}}$$

$$\text{Sh} = 1.45 \cdot (\text{Re})^{0.32} (\text{Sc})^{0.33}$$

$$\text{Re} = \frac{r\, v_g D_{membr}}{h} \quad \text{and} \quad Sc = \frac{h}{r\, Diff}$$

$$v_g = \frac{f_v}{A_{cross}}$$

For themembranewall

$$k_m = \frac{\text{Perm} \cdot \text{H}}{R_{averaged}}$$

$$R_{averaged} = R_{ex} \cdot \ln\left(\frac{\text{R}_{ex}}{R_{in}}\right)$$

$$\frac{1}{k} = \frac{1}{k_m} + \frac{1}{k_l}$$

The Reynolds number can be calculated on basis of the mixing pattern caused by sparged air in to a liquid [data companion].

Mass balances for gas transfer over the bubbles

The bubble column is a commonly used bioreactor for two-phase systems. It is commonly known that design of bubble columns is attained to a high number of variables (liquid properties, height and width of the column, sparger, internal structures, etc); the main consequence of this is the high unreliability of the calculations. In practice bubble columns are designed within reliability boundaries and before construction starts experiments are done to reduce this uncertainty.

Appendix 2-3: Mass and heat balances for the calculation of the dimensions of the reactor

Mass balance per component (i) over the gas phase

$$0 = \mathrm{in}_i - \mathrm{out}_i - \mathrm{transfer}_i$$

$$0 = f_v C_{g,i}\big|_x - f_v C_{g,i}\big|_{x+dx} - k_l a \cdot (C^*_{g,i} - C_{l,i}) \cdot A_c \Delta x$$

$$C_{l,O2} \approx 0$$

$$\frac{d(f_v C_{g,i})}{dx} = -A_c \cdot k_l a\left(\frac{C_{g,i}}{m_i} - C_{l,i}\right)$$

$$C_{g,i}\frac{df_v}{dx} + f_v\frac{dC_{g,i}}{dx} = -A_c \cdot k_l a\left(\frac{C_{g,i}}{m_i} - C_{l,i}\right)$$

$$\frac{dC_{g,i}}{dx} = \frac{-A_c \cdot k_l a\left(\frac{C_{g,i}}{m_i} - C_{l,i}\right) - C_{g,i}\frac{df_v}{dx}}{f_v}$$

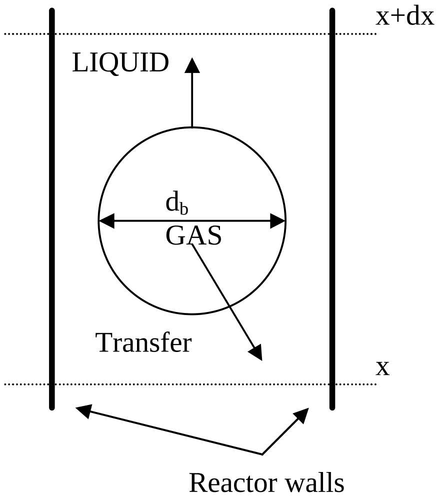
t

$$C_{g,i} = \frac{Mass}{Volume} = \frac{y_{in,i} \cdot P}{R \cdot T \cdot Mn_i}$$

The concentration in the liquid phase is assumed to be negligible, because of the high consumption rate compared to the mass transfer rate. The interfacial gas concentration is calculated with Henry’s law.

Total Mass balance over the gas

0=in-out-transfer



$$0 = f_{mol}\Big|_{x} - f_{mol}\Big|_{x+dx} - \sum k_l a \cdot (C^*_{g,i} - C_{l.i}) \cdot A_c \Delta x$$

$$C_{l,O2} \approx 0$$

$$\frac{df_{mol}}{dx} = -A_c \cdot \sum k_l a \left(\frac{C_{g,i}}{m_i \cdot Mn_i} - C_{l,i} \right)$$

$$\frac{df_{mol}}{dx} = \frac{d\left(\frac{f_v P}{RT}\right)}{dx} = \frac{1}{RT}\frac{d(f_v P)}{dx} =$$

$$P\frac{df_v}{dx} + f_v\frac{dP}{dx} = -\frac{A_c}{RT} \cdot \sum k_l a \left(\frac{C_{g,i}}{m_i \cdot Mn_i} - C_{l,i} \right)$$

$$\frac{df_v}{dx} = \frac{-A_c \cdot R \cdot T \cdot \sum k_l a \left(\frac{C_{g,i}}{m_i \cdot Mn_i} - C_{l,i} \right) - f_v \frac{dP}{dx}}{P}$$

Where the pressure profile over the height of the reactor can be calculated as follows:

$$P = P_t + (1 - e_m) \cdot r \cdot g \cdot (H_c - x)$$

$$\frac{dP}{dx} = -(1 - e_m) \cdot r \cdot g$$

The mass transfer coefficients are calculated by means of the Sherwood number [Janssen 1997]

$$k_l = sh\frac{Diff}{d_b}$$

$$sh = 2 + 0.66\,(\mathrm{Re})^{0.5}\,(Sc)^{0.33}$$

$$\mathrm{Re} = \frac{r\, v_g d_b}{h} \qquad and \qquad Sc = \frac{h}{r\, Diff}$$

$$v_g = \frac{f_v}{A_c}$$

2.3.3 Heat balances

The heat balances over the reactors are quite simple. In biological reactors the heat produced is mostly assumed to be equal to the heat produced by the catabolic reaction. In this case the catabolic reaction is constituted by two reactions, since alcaligenes eutrophus is able to utilise H_2 and CO for energy production at the same time [Schlegel, 1997]. From the heat balance it follows that a device is required to keep the temperature inside of the reactor constant. In this case the heat to be removed is quite low, but due to quality measures (constant production rate, etc) a heat jacket is incorporated to the reactors.
The overall heat balance is as follows:

$$f_w = \sum_{i=Sg,air,liq} f_{m,i,in} \cdot H_{i,in} - \sum_{i=Sg,air,liq} f_{m,i,uit} \cdot H_{i,uit} - f_{m,vap} \cdot ?H_{vap} + f_{m,cat} \cdot (-?H_r)$$

$$\sum_{i=Sg,air,liq} f_{m,i,in} \cdot H_{i,in} = f_{m,l,in} H_{l,in} + f_{m,sg,in} H_{sg,in} + f_{m,a,in} H_{a,in}$$

$$\sum_{i=Sg,air,liq} f_{m,i,uit} \cdot H_{i,uit} = -f_{m,l,out} H_{l,out} - f_{m,sg,out} H_{sg,out} - f_{m,a,out} H_{a,out}$$

The heat of reaction is calculated on basis of the amount of hydrogen and carbon monoxide that is transferred and consumed by the micro-organisms for catabolism.

$$f_{m,cat} ?H_r = mass\,tranf\ H_2 \cdot ?H_{r,H_2+\frac{1}{2}O_2} + mass\,tranf\ H_2 \cdot ?H_{r,CO+\frac{1}{2}O_2}$$

From this balance it follows that heat has to be removed. Therefore, as stated before, a simple cooling jacket is designed.

$$f_w = UA(T_{cooling} - T_r)$$

$$UA = \frac{f_w}{(T_{cooling} - T_r)}$$

$$U = \frac{UA}{A_{jacket}}$$

$$\frac{1}{h_{jacket}} = \frac{1}{U} - \left(\frac{1}{h_{wall}} + \frac{1}{h_{internal}}\right)$$

$$h_{internal} = \frac{l_{water}}{Dk} * 0.027 \cdot \mathrm{Re}^{0.8} \cdot \mathrm{Pr}_{binnen}^{0.33}$$

$$h_{wall} = \frac{l_{steel}}{d_{wall}}$$

$$j_{heat,jacket} = \frac{Nu}{\mathrm{RePr}^{0.33}} = 0.0845 \cdot \left(\frac{\mathrm{w}}{\mathrm{x}}\right)^{0.368} \cdot \left(\frac{\mathrm{A}_{\min}}{\mathrm{A}_{\max}}\right)^{0.383} \cdot \mathrm{Re}^{0.305}$$

$$\mathrm{Re}\ j_{heat,jacket} = \frac{h_{jacket} \cdot d_0}{l_{water}\,\mathrm{Pr}^{0.33}}$$

$$d_0 = \frac{(d_1 + d_2)}{2}$$

$$A_{\min} = z \cdot (x - d_0) \qquad A_{\max} = z \cdot x$$

$$\mathrm{Re} = \frac{\mathrm{Re}\ j_{heat,jacket}}{j_{heat,jacket}}$$

$$v_{max} = \frac{\mathrm{Re} \cdot h_w}{d_0\, r_w}$$

$$n_{dimples} = \frac{H_{jacket}}{w}$$

$$f_{v,cooling,dimple} = v_{max} \cdot A_{min}$$

$$f_{v,cooling} = f_{v,cooling,dimple} \cdot n_{dimples}$$

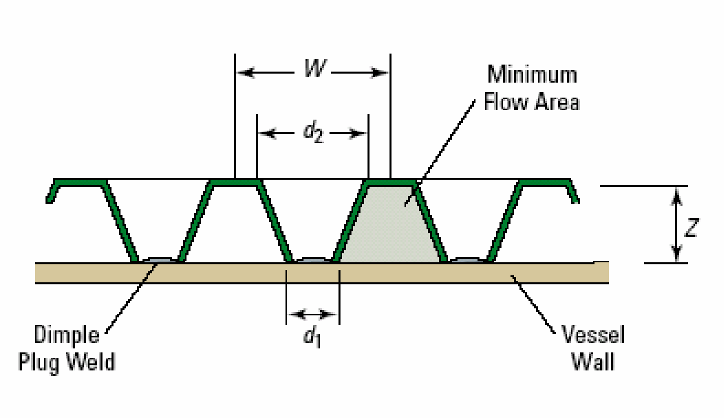


Figure 2: Schematic presentation of the cooling jacket. Garvin, J. Estimate heat transfer and friction in dimple jackets. Sprinfield, 2001. http://www.cepmagazine.org

Appendix 2-3: Mass and heat balances for the calculation of the dimensions of the reactor

2-4 Nutrients

Except for the carbon and energy source the bacteria require nutrients. The main nutrient components required are a nitrogen, sulphur and phosphate source. Furthermore trace elements are required as minerals and vitamins. Only the main nutrients will be worked out, whilst the trace elements are neglected concerning their low requirement.
The growth and production reactor require different amount of nutrients. The growth reactor requires the amount of nutrient fixed in the biomass. The production reactor is nitrogen limited, since little nitrogen addition gives higher PHB production [Heijnen 2003]. The reason for this is that certain maintenance processes require nitrogen. The production reactor also requires other nutrients in order to perform maintenance reactions. The nutrients added to the production reactor are neglected, since the required amount is far less than in the growth reactor. Furthermore little data is available on the nutrient requirement under growth limiting conditions.

For the growth reactor the required elemental nitrogen and phosphor per gram of biomass is around 0.11 gram and 0.012 grams respectively [Heijnen 2003]. No data is available on the amount of sulphur needed, thus it is assumed that this is about the same amount as the amount of phosphate needed. Together with the microbial production rate the required nutrients can be calculated.

In the reactors the syn-gas stream will provide part of these nutrients. The reason for this is that in the gasifier substances are produced which are suitable as nutrient source, like nitrates, ammonia and hydrogen sulphite. The concentrations of these substances in the syn-gas are very low, whilst their solubilities in water are often very high. Therefore it is very difficult to give an estimation of the amount of nutrients transferred. Thus it is assumed that all nutrients have to be provided from another source.
Ammonium will be used as the nitrogen source, since it is a commonly used salt in fermentation industry. As sulphur source ammonium sulphate will be used and as phosphor source di-ammonium phosphate will be used. The latter are chosen since different ammonium salts are in the same price range, thus in this way phosphor and sulphur are provided together with the ammonia. The remainder of the nitrogen that has to be provided is delivered through ammonium nitrate. The latter substance is also in the same price range as other ammonium salts, but delivers two moles of nitrogen per mole of substance. The required amounts as well as the prices and costs of the nutrients are given in Table 1.[Bioclean Impex 2004]

Table 1: Elemental requirements of the main nutrients for growth

Element	Requirement	Unit
Nitrogen	$1.39 \cdot 10^{-03}$	[kg/s]
Phosphor	$1.52 \cdot 10^{-04}$	[kg/s]
Sulphur	$1.52 \cdot 10^{-04}$	[kg/s]

Table 2: Required nutrient sources for the growth reactor and their costs

Nutrient source	**Requirement [kg/yr]**	**Price in [€/kg]**	**Annual costs [€/yr]**
Ammonium nitrate	97.000	0.25	24.500
Di-ammonium phosphate	19.000	0.25	3.600
Ammonium Sulphate	18.000	0.19	4.700
Total	**134.000**	**0.69**	**32.800**

The nutrients will be provided by making defined concentrated solution in a small vessel. This vessel is emptied in a storage vessel, which will continuously add the nutrient stream to a mixer. This mixer mixes the water stream to the growth reactor with the nutrient solution.
All nutrients are soluble in water, thus concerning its relative amount the component determining the storage vessel size will be ammonium nitrate. The maximum solubility of ammonium nitrate is 208 g per 100 grams of water [Wikipedia 2004]. It is assumed that the storage vessel should have enough nutrients to provide the reactor for approximately 1.5 days. The vessel thus becomes 2 m^3.
The dimensions of the mixer are neglected, because of the small nutrient stream relative to incoming growth reactor stream.

2-5 Design and Matlab model description

2.5.1 Design

The reactor is designed the following way. For a certain mass transfer in the reactor a certain membrane volume is required, which is independent of the amount of membranes. The membranes should fully contact the liquid and also sparging of bubbles between the membranes must be possible, thus there exists a maximal membrane hold-up (membrane volume divided by the total volume) for which this is still possible. This maximum membrane hold-up is estimated be 0.5. This estimate was made by examining the membrane bioreactors used in some waste water treatment plants for the suction cleaned water. In figure 10 and figure 9 a membrane unit is shown produced by the company Zenon. With the membrane hold-up and the acquired membrane volume a reactor volume is calculated. The volume not occupied by me is occupied by the liquid and gas phase. It is assumed that the gas will not be directly in contact with the membranes, since mostly a liquid film layer is formed between the membranes and the gas phase. With the volume available for the liquid and the gas phase the bubble column is designed. The bubble column will have the form of a cylinder for better mixing properties. The initial gas flowrate and the ratio of height and diameter of the reactor are varied in order to get the required mass transfer in oxygen. The average final gas hold-up (volume of gas divided by the liquid volume) should however be around 20, since higher hold-ups will give to much coalescence of the bubbles. If the required mass transfer can however not be reached this requirement a lower membrane hold up must be taken. The design of the bubble column will give the column or reactor height. This height will also be the membrane length, with this membrane length the amount of required membranes is calculated. The reactor is drawn in figure 3 of Appendix 2-2

Figure 1:Membranes with housing as produced by Zenon (www.zenon.com)

Figure 2: Single cassette which can be taken from the housing (www. Zenon.com)

2.5.2 Model description

The balances derived in appendix 2-3 are solved using the technical computation program matlab, because solving the equations manually is extremely complicated and requires much time. Matlab is a computation program in which one is free to write his own computational script. Several scripts or function are predefined. The predefined functions mainly used for this model are integration functions and iteration functions.

The scripts written can be seen in appendix 2-6. In the scripts the various mathematical operations are explained. Furthermore the file gives the various literature sources from which constants and relations are taken. The backbone of the script will however be discussed shortly in this.

The script written is devided into several function files. The main file contains all the inputs and outputs required as well as the iterative procedures, this file is called "growth_react.m" for the growth reactor and "prod_react" for the production reactor. The main file will explained further on. The other files will be discussed shortly below:

- MBBM.m: This file has as an input the cell concentration and the ratio of the transferred hydrogen and carbon monoxide. With the balance over the biomass and the stoichiometric relations it calculates and returns the required PHB or biomass production rate, the liquid flowrate through the reactor, the yields of PHB or biomass on the various substances consumed and produced and the required mass transferred rate of the various substances which are to be transferred.
- Syg_Dat.m: This file has as an input the temperature of the reactor, the viscosity of the liquid and the pressure of the synthesis gas. It returns data required for the diffusion of the different substances in syn-gas through the membranes. The returned values are the dimensionless Henry coefficients as well as the Henry coefficients expressed in $m^{3\cdot}$Pa/mol, the molar masses, the membrane permeabilities and the liquid diffusities.
- Ox_Dat.m: This file has as an input the temperature of the reactor and the viscosity of the liquid. It returns data required for the diffusion of oxygen and nitruogen from the bubbles to the liquid. The returned variables are [ma Mna DifLa] the dimensionless henry coefficients, the molar masses and the liquid diffusities.
- Derimc.m: This file contains the mass balances over the membranes derived in appendix 2-3. This file is used by an integration solver of matlab. As an input the file has the boundary conditions used to solve the mass balances as well as all the constants used in these balances. The returned variables are the solved integration variables, namely the concentration profiles over the membrane length as well as the flowrate profile over the membrane length
- Deriv.m: This file contains the mass balances over the bubbles as derived in appendix 2-3. This file is used by an integration solver of matlab. The output of this file is used create an initial guess value for the gas hold-up profile in the column. The returned variables are the solved integration variables, namely the gas concentration profile through the column, the gas flowrate through the column and the pressure profile through the column.
- Deriv2.m: This file also contains the mass balances over the bubbles and is also used by an integration solver of matlab. This file however uses the initial guess value created as explained above. The output of the file is the same as for Deriv.m.

The main file starts with loading all necessary variables for solving the mass balances. The first balances to be solved are those over the membranes. As explainde above the the file firstly calculates a membrane surface required, which is constant for a certain mass transfer. The length of the membranes thus doesn't influence the concentration profile. Figure 11 and figure 12 give the molar concentration profile through the memrbanes of the production and growth reactor respectivily.

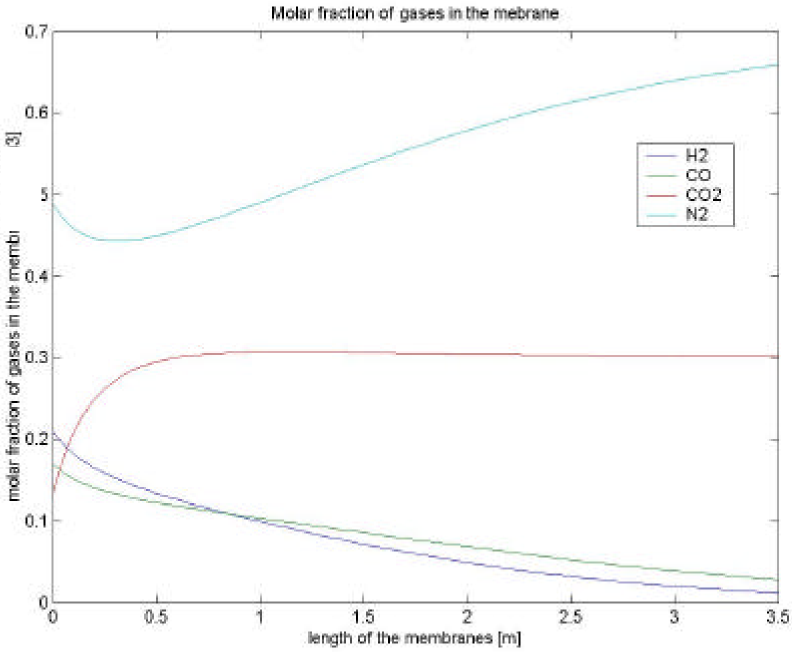


Figure 3: Molar concentration profile through the membranes of the production reactor

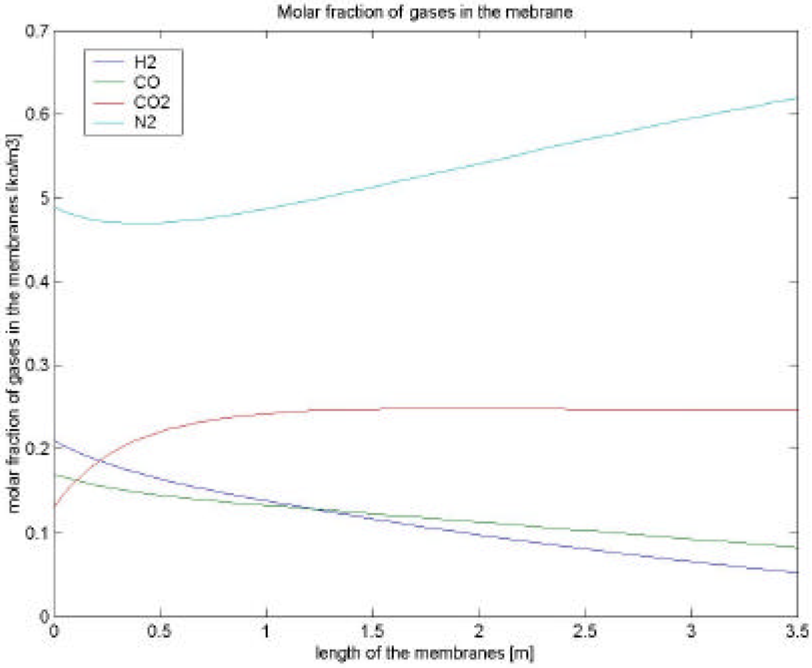


Figure 4: Molar concentration profile through the membranes of the growth reactor

As can be seen the concentrations of carbon monoxide and hydrogen in the producution are so low that more membrane surface would not contribute significantly to more mass transfer. The amount loss of substrate in the production reactor (~8% of incoming substrate) thus is acceptable. In the production reactor however concentrations of hydrogen and carbon monoxide are still relatively low. Less syn-gas could be provide to this reactor in order to lower the loss. There was however not enough time to correct this.

As stated above the membrane surface determines the reactor size through the membrane hold-up. With the volume available for liquid and gas the bubble column is designed. The concentration profile of oxigen and nitrogen through the column is given in figure 13 and figure 14 for the production and growth reactor respectivly.

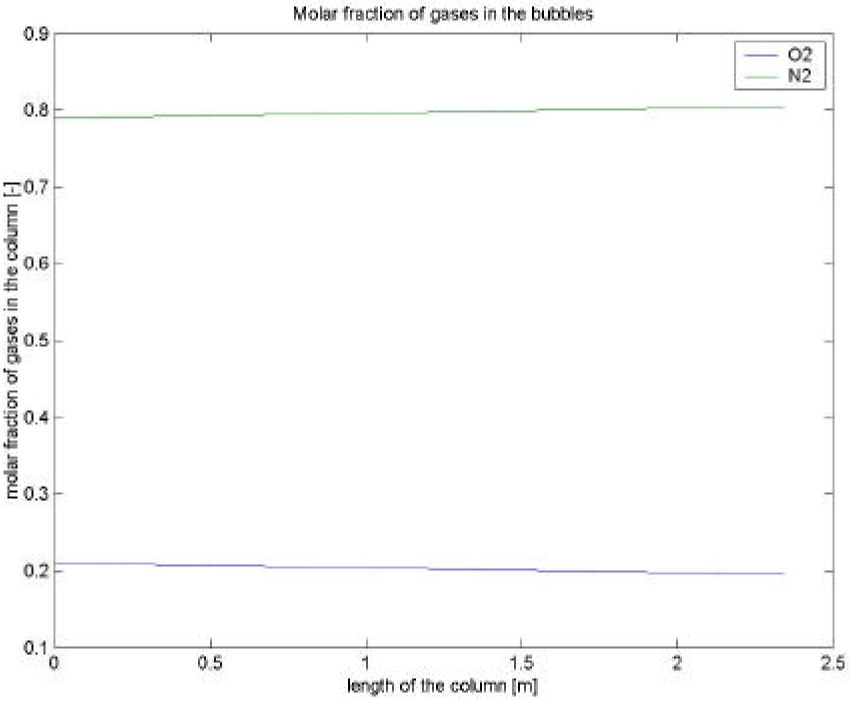


Figure 5: Molar concentration profile through the column of the production reactor

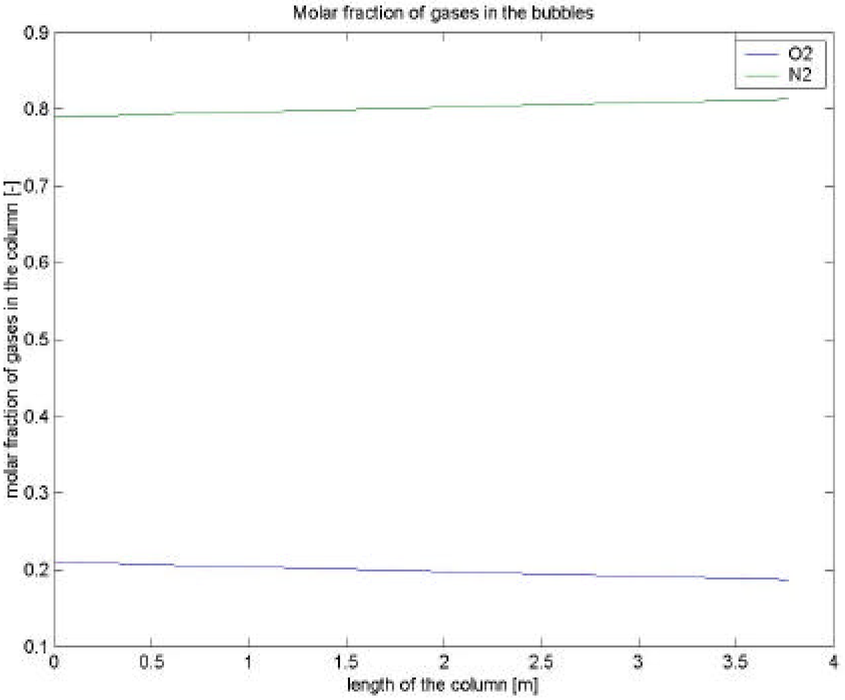


Figure 6:Molar concentration profile through the column of the production reactor

As can be seen both reactor have about the same concentration profile. Driving forces for oxigen transfer are low and as can be seen from both figures very few oxigen is transferred. Air is however a cheap substrate and therefore there is no reason to improve the mass transfer of oxigen.
From here on the number of membranes is manually calculated by varing the latter untill the membrane length is equal to the column height.
At the ending of the file the heat balances are worked out with as a result the flowrate of the cooling medium (water).

Further details, literature and assumption are given in the main file itself as comment and can be found in appendix 2-6.

```
%   Appendix 2-6:   Matlab scrips Fermentation
%            2-6-1  Design of the Production Reactor

%   File for the calculations of the dimension of the production reactor

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%      Fermentor calculations      %%
%%      Cpd3310 Production of PHB   %%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%   This file calculates the dimensions and operation characteristics of a
%   membrane bioreactor. It is divided in three sections: One for the
%   calculation of the required membrane surface to achieve the required
%   production of PHB. A second section where the dimensions of the reactor
%   are calculated accoording to the volume of the membranes, liquid and
%   gas bubbles.
%   Finally the energy balance is solved and the required cooling jacket
%   surface is calculated.

%   This file utilises 6 other files. 2 files for data of synthesis gas and
%   air gas. In this files permeabilities, diffusivities, etc are given. 1
%   file for the stoichiometric data of the reactions and 3 files
%   containing the mass balances, 2 of those are for the membrane surface
%   calculation and 1 for the reactor dimensions.


clear all               % clear variables in work space
format long e           % Floating point format with 15 digits.
clc                     % clear screen

%   CONSTANTS
g=9.81;                 %   [m2/s]      Gravity aceleration
R=8.3415;               %   [SI-units]  Gas constant
rho=1000;               %   [kg/m3]     density of broth
vis=0.001;              %   [kg/ms2]    viscosity of broth
Mw=18e-3;               %   [kg/mol]    Molecular weight of water

%   Conditions in the reactor and membranes
Tr=30+273;              %   [K]         Temperature of the reactor and gases
Psg=10*101325;          %   [Pa]        Pressure of the inlet synthesis gas
Pt=5*101325;            %   [Pa]        Pressure on the top of the reactor


Re=10000;                %   [-]         Reynolds number (from some table in the data
compainon)

% Inlet conditions
Tsg_in=40+273;           %   [K]     temperature of the synthesis gas into the reactor
Tliq_in=40+273;          %   [K]     temperature of the liquid
Ta_in=20+273;            %   [K]     temperature of the air (outside)
Tomgv=20+273;            %   [k]     temperature of the outside

% Composition of the synthesis gas in volume or molar fraction
yinH2=0.21;                                     %   [-]     Molar fraction H2 in
inflow
yinCO=0.17;                                     %   [-]     Molar fraction CO in
inflow
yinCO2=0.13;                                    %   [-]     molar fraction of CO2 in
inflow
yinN2=1-yinH2-yinCO-yinCO2;                     %   [-]     Molar fraction of N2 in
inflow
ysgin=[yinH2; yinCO; yinCO2; yinN2];            %   [-]     Vector containing the
molar fraction of SynGas

% Data on synthesis gas.

% For this the file Syg_Dat is
% called. This file has as inputs the temperature of the synthesis gas
% (equals the reaction temperature) the synthesis gas pressure and the
% viscosity of the liquid respectively. It return a matrix Sg_dat=[msg
% H Mnsg Perm DifL]. These are in respective order the dimensionless henry coefficient,
the
```

```
% henry coefficient in m3*Pa/mol, the molar mass, the permeability through the
% membranes and finally the liquid diffusities. The rows represent the
% substances, in respective order H2;CO;CO2.


SGConditions=[Tr; Psg;vis];                  %                  initiate input
vector (improvement compared to MBBM.m)
syn_data=Syg_Dat(SGConditions);              %                  Call function file
msg=syn_data(:,1);                           %   [-]            dimensionless Henry
coefficient
H=syn_data(:,2);                             %   [m3*Pa/mol]    Henry coefficient
Mnsg=syn_data(:,3);                          %   [kg/mol]       molar mass
substances Syngas
Perm=syn_data(:,4);                          %   [mol/(s-m-Pa)] Permeability through
the membranes
DifL=syn_data(:,5);                          %   [m2/s]         Liquid diffusities

% Composition of air in gas volume or molar fraction
yinO2=0.21;                                 %   [-]     Molar fraction oxygen inflow
yinN2=1-yinO2;                              %   [-]     Molar fraction of nitrogen
in inflow
yain=[yinO2; yinN2];                        %   [-]     Vector containing fraction
of the substances in air
Csg_0=ysgin.*(Psg/(R*Tr)).*Mnsg;            %   [kg/m3] Concentration of Nitrogen in
gas phase

%Synthesis gas flow rate
Fmsg0=3700/3600  ;                          % [kg/s]  Synthesis gas flowrate coming
from the reactor
Fmolsg0=Fmsg0/(ysgin'*Mnsg);                % [mol/s] Synthesis gas flowrate coming
from the reactor
splitfact=3/4 ;                             %         Part of the delivered
synthesis gas going to the production reactor
Fvsg0=((Fmolsg0*splitfact)*R*Tr)/(Psg);     % [m3/s]  Air flow into the reactor

% Data on air.

% For this the file Ox_Dat is called. It does essentially the same as
% Syg_Dat. The inputs are the temperature in the reactor and the viscosity
% of the liquid respectively. It returns a matrix Oxg_dat=[ma Mna DifLa].
% These are in respective oreder the dimensionless henry coefficient, the
% molecular weight and the Liquid diffusities. The rows represent the
% substances, in respective order O2;N2.

OXConditions=[Tr;vis];                      %               Initiate input vector
Oxyg_data=Ox_Dat(OXConditions);             %               Call function file
ma=Oxyg_data(:,1);                          %    [-]        Henry coefficients
Mna=Oxyg_data(:,2);                         %    [kg/mol]   Molar mass
DifLa=Oxyg_data(:,3);                       %    [m2/s]     Diffusities

% Data on membranes

%   Data on membranes
%   the amount of membranes is a variable input!
Rmi=0.75e-3;                                %   [m]     External radius of the
membranes
n=2000000

;                                           %   [-]     number of membranes
thick=25e-6;                                %   [m]     Thickness of a membrane
Rme=Rmi+thick;                              %   [m]     Internal radius of the
membranes
hlm=0.5;                                    %   [-]     Space occupyed by the
membranes in the reactor
Rcyl=Rme*log(Rme/Rmi);                      %   [m]     Equivalent radius of the
membranes
Diam=2*Rme;                                 %   [m]     Averaged diameter of the
membranes

%   MEMBRANE MASS TRANSFER COEFICIENTS CALCULATIONS
Sc=vis./(DifL.*rho);                     %   [-]       Smidt number
Sh=1.45.*(Re.^0.32)*(Sc.^0.33);          %   [-]       Sherwood
```

```
klm=Sh.*DifL./(2.*Rme);                     %   [m/s]     Mass transfer coefficient
liquid on the membrane surface
km=Perm.*H./Rcyl;                           %   [m/s]     Mass transfer coefficient
membranes
k=1./((1./km)+(1./klm));                    %   [m/s]     Overall mass transfer
coefficient membranes


%   Here starts the iteration procedure

% start iteration procedure for finding minimum mebrane length
RAT=1.5;                                   %           initial consumed ratio
Lm=8;                                      %   [m]     initial Length of the single
membranes
differ_Lm=10;                              %           make sure iteration starts
precision=1                                %   [m]     precision of the iteration
(required min difference between
                                           %           given membrane length and best
guess value)
while differ_Lm>precision                  %   [m]     Persicion of the membrane length
calculation

    % Contraint DATA
    % Calling required mass transfer requirements by using the funtion file
    % MBBM. As input the file has a final concentration of the biomass with
    % PHB and a consumption ratio of H2 over CO. The file returns a matrix
    % called constraints=[PhiL;MTR2;YiPHB;P_PHB], With first column of Phil
    % is the liquid flowrate through the reactor and rest of the columns is
    % zero, MTR2 is the required consumed H2 CO CO2 and O2 (these are the
    % columns in respective order) for a given ratio, the yields of PHB on
    % the synthesis gas (H2, CO, CO2, O2 for the columns respectively) and
    % finally the required production of PHB with the last three columns
    % equal to zero

    Constraints=MBBM(200,RAT);                        %   Call funtion file for
constraints
    MTR2=Constraints(2,:);                            %   [kg/s]  REquired mass
transfer (H2 CO CO2 O2) to the production reactor
    Fvliq=Constraints(1,1);                           %   [m3/s]  Volumetric flow
stream
    MTR2sg=MTR2(1:3)';                                %   [kg/s]  Vector with the
required mass tranfer of SynGas [H2;CO;CO2]
    MTR2a=MTR2(4);                                    %   [kg/s]  Vector with the
required mass transfer of oxigen in air
    YiPHB=Constraints(3,:);                           %   [kg/kg] Yield for PHB
production on H2 CO CO2 O2 respectivily
    P_PHB=Constraints(4,1);                           %   [kg/s]  Expected PHB
production in the reactor

    % ODE solver settings
    options = odeset('RelTol',1e-4,'AbsTol',1e-4);    %     error tolerances of the
solver

    % Initial conditions for the solver
    % VARM is the vector containing the to be integrated variables.
    % [C_H2_0;C_CO_0;C_CO2_0;C_N2_0;Fv_0]
    z0=0;
    zf=Lm;
    zspan = [z0 zf];                            %   vector containing integration
domain
    VARM0=[Csg_0;Fvsg0];                        %   [-]     Initial conditions

    % Iteration procedure to find the liquid CO2 concentration at the given membrane
length

    % Iterative steps to calculate the liquid concentration of carbon dioxide. An
amount of
    % 'steps' values for the liquid  concentration are filled in starting at begin and
ending
    % at at begin+delta. For al steps the final liquid concentration is % calculated
with
    % Cl=(prod+trans)/Fvliq. The absolute least difference between the cl input and cl
```

```
calculated
    % is found and in the next iterative loop the filled in concentration starts at
value input
    % previous of the min cl difference and ends at the next. The loop stops when the
min
    % difference is smaller than error and finally returns the value of the
    % liquid concentration of carbon dioxide

    error=1e-4;                     % difference required between given liquid CO2
concentration and the calculated
    a=error+1;                      % initial difference to start procedure
    steps=100;                      % amount of points investigated per iteration
    begin=0.5;                      % initial first gues or beginning point of the
liquid CO2 concentration
    delta=10;                       % initial difference between the beginning liquid
concentration and the final one
    ClgCO2=zeros(steps,1);          % initiate vector containing the values of the
calculated liquid concentration

    while a>error ;
        for i=1:steps

            ClgCO2(i,1)=begin+(delta/(steps-1))*(i-1) ;     % vector containing given
liquid phase concentrations
            Clg=[0;0;ClgCO2(i)];                            % vectror containing all
liquid phase concentrations for the iteration

            %Call ODE solver:
            [z,VARM] = ode45 ('derimc', zspan, VARM0,
options,Diam,n,k,msg,R,Tr,Psg,Mnsg,Clg); % call integration procedure

            m_t_CO2=Fvsg0*Csg_0(3)-VARM(length(z),5)*VARM(length(z),3); % [kg/s]
amount of CO2 transfered
            m_t_CO=Fvsg0*Csg_0(2)-VARM(length(z),5)*VARM(length(z),2);  % [kg/s]
amount of CO transfer
            prodCO2=(m_t_CO/Mnsg(2)-4*P_PHB/86e-3)*Mnsg(3);             % [kg/s]
amount of CO2 produced. NB 86e-3 is molar mass of PHB
            ClCO2calc(i,1)=(m_t_CO2+prodCO2)/Fvliq;                     % [kg/m3]
Caclulated liquid CO2 concentration


        end

        difference=abs(ClCO2calc-ClgCO2);       % calculate the absolute diffences
between the given and calculated liquid CO2 concentration
        [a b]=min(difference);                  % Find the minimum diffence and return
a the value and b the row number
        begin=ClgCO2(b-1);                      % give new beginning point for the
given CO2 concentrations. This points is the given point before the min difference
point
        delta=ClgCO2(b+1)-ClgCO2(b-1);          % state that the next run should end at
the point next to the min difference point

    end

    % Return the found values from the previous iteration procedure
    ClgCO2fin=ClgCO2(b)
    Clg=[0;0;ClgCO2fin];

    % Perform integration with found values to give answers
    [z,VARM] = ode45 ('derimc', zspan, VARM0, options,Diam,n,k,msg,R,Tr,Psg,Mnsg,Clg);
% call integration procedure

    % Transform answers in a workable form
    Fsvg_in=VARM(1,5);
    Fsvg_z=VARM(:,5);       %   [m3/s]        Flowrate through the membrane
    CgH2_z=VARM(:,1);       %   [kg/m3]       Concentration of hydrogen through the
membrane
    CgCO_z=VARM(:,2);       %   [kg/m3]       Concentration of CO through the membrane
    CgCO2_z=VARM(:,3);      %   [kg/m3]       Concentration of CO2 through the membrane
    CgN2_z=VARM(:,4);       %   [kg/m3]       Concentration of N2 through the membrane
```

```
    % calculate the mass transfer of H2 and CO through the column
    mtH2z=-Fsvg_z.*CgH2_z+Fsvg0*Csg_0(1);   %   [kg/s]  hydrogen
    mtCOz=-Fsvg_z.*CgCO_z+Fsvg0*Csg_0(2);   %   [kg/s]  Carbon monoxide

    %calculate the final mass transefer
    mtH2=Fvsg0*Csg_0(1)-Fsvg_z(length(z),1)*CgH2_z(length(z));  %   [kg/s]  hydrogen
    mtCO=Fvsg0*Csg_0(2)-Fsvg_z(length(z),1)*CgCO_z(length(z));  %   [kg/s]  Carbon
monoxide
    mtCO2=Fvsg0*Csg_0(3)-Fsvg_z(length(z),1)*CgCO2_z(length(z));%   [kg/s]  Carbon
dioxide
    mtN2=Fvsg0*Csg_0(4)-Fsvg_z(length(z),1)*CgN2_z(length(z));  %   [kg/s]  Nitrogen

    % required mass transfer rates of H2 and CO
    mtH2req=MTR2sg(1);                                          %   [kg/s]  hydrogen
    mtCOreq=MTR2sg(2);                                          %   [kg/s]  Carbon
monoxide

    % Check if there is enough mass transfer. If  negative, not enough
    % mass transfer, if positive their is enough mass transfer
    SignH2=sign(mtH2-mtH2req);
    SignCO=sign(mtCO-mtCOreq);

    % Calculate the difference throught the column between the actual and
    % required mass transfer
    mtdifferH2z=mtH2z-mtH2req;
    mtdifferCOz=mtCOz-mtCOreq;

    % find the minimum difference between required and actual and return the row of z
at that difference
    [mtbestH2 zH2]=min(abs(mtdifferH2z));
    [mtbestCO zCO]=min(abs(mtdifferCOz));

    % Statements for next iteration cycle

    % If the there is not enough mass transfer enlong the membrane length
    % with 3 meters.
    if SignH2<0 | SignCO<0;
        Lmcalc=Lm
        Lm=Lm+3;                            % give new membrane length
        RAT=(mtH2*28)/(mtCO*2);             % give new best guess for the consumed
ratio (ratio at end of membrane)
        disp('not enough mass transfer');

    % If H2 is limiting
    elseif zH2>zCO;
        differ_Lm=Lm-z(zH2)                             % Calculate the diffence
between the given membrane length and the best gues
        Lmcalc=Lm                                       % Save the latest membrane
length
        Lm=Lm-precision/2;                              % If necessarry the next cycle
will use membranes 1 meter shorte
        [RowzNP]=find(z>(Lm-precision/2));              % Find the row in z for the
next membrane length
        RAT=(28*mtH2z(RowzNP(1)))/(2*mtCOz(RowzNP(1))); % Calculate the guess ratio for
the next given membrane length
        disp('H2 is limiting');

    % If CO is limiting
    else
        differ_Lm=Lm-z(zCO)
        Lmcalc=Lm
        Lm=Lm-precision/2;
        [RowzNP]=find(z>(Lm-precision/2));
        RAT=(28*mtH2z(RowzNP(1)))/(2*mtCOz(RowzNP(1)));
        disp('CO is limiting')
    end
end

% define losses of substrate.
loss=100*(Fsvg_z(length(z),1)*CgH2_z(length(z))+Fsvg_z(length(z),1)*CgCO_z(length(z)))/
((Fvsg0*Csg_0(1))+(Fvsg0*Csg_0(2)));
COloss=100*(Fsvg_z(length(z),1)*CgCO_z(length(z)))/(Fvsg0*Csg_0(2));
```

```
%   Membrane and reactor characteristics

Sm=2*pi*Rme*Lm*n;                       % [m2]      Total surface area of the membranes
Vm=pi*(Rme^2)*Lm*n;                     % [m3]      Volume of the membranes
Vr=Vm/hlm;                              % [m3]      Total reactor volume

disp('characteristics of the membrane bioreactor')
Dimensions_Sm_Vm_Vr=[Sm Vm Vr]

% Figures

figure(1);
plot(z,mtH2z,z,mtCOz);
title('mass transfer through the membrane');
xlabel('length of the membranes [m]');
ylabel('transfered gas [kg/s]');
legend('H2','CO');

figure(2)
plot(z,VARM(:,1:4));
title('concentrations of the gasses in the mebranes');
xlabel('length of the membranes [m]');
ylabel('concentration of gases [kg/m3]');
legend('H2','CO','CO2','N2');

figure(3)
plot(z,VARM(:,5));
title('volume flow rate through the membranes');
title('volume flow rate');
xlabel('length of the membrane [m]')
ylabel('volume flowrate [m3/s]')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%    calculation of the molar and mass fractions %%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%  SYNTHESIS GAS:  MOLAR FRACTIONS calculations
CgH2sg_mol_z=CgH2_z./Mnsg(1);       %   [kg/m3] Concentration H2 over the length of the
membranes
CgCOsg_mol_z=CgCO_z./Mnsg(2);       %   [kg/m3] Concentration CO over the length of the
membranes
CgCO2sg_mol_z=CgCO2_z./Mnsg(3);     %   [kg/m3] Concentration CO2 over the length of
the membranes
CgN2sg_mol_z=CgN2_z./Mnsg(4);       %   [kg/m3] Concentration N2 over the length of the
membranes
Cgsg_tot_z=CgH2sg_mol_z+CgCOsg_mol_z+CgCO2sg_mol_z+CgN2sg_mol_z;    %   [kg/m3] Total
concentration

%   Molar fractions over the length of the membranes of H2, CO, CO2, N2
yH2_mol_z=CgH2sg_mol_z./Cgsg_tot_z;     %   [-] H2
yCO_mol_z=CgCOsg_mol_z./Cgsg_tot_z;     %   [-] CO
yCO2_mol_z=CgCO2sg_mol_z./Cgsg_tot_z;   %   [-] CO2
yN2_mol_z=CgN2sg_mol_z./Cgsg_tot_z;     %   [-] N2
ysg_mol_z=[yH2_mol_z yCO_mol_z yCO2_mol_z yN2_mol_z];

mtH2zmol=-Fsvg_z.*CgH2sg_mol_z+Fvsg0*Csg_0(1);
mtCOzmol=-Fsvg_z.*CgCOsg_mol_z+Fvsg0*Csg_0(2);


figure(4); plot(z,yH2_mol_z,z,yCO_mol_z,z,yCO2_mol_z,z,yN2_mol_z);
title('Molar fraction of gases in the mebrane');
xlabel('length of the membranes [m]');
ylabel('molar fraction of gases in the membranes [kg/m3]');
legend('H2','CO','CO2','N2');


%Calculating the exact dimensions of the reactors
Vr=Vr/3;
npr=n/3;

%   Characteristics for the bubble column
hldgem=0.2;                                 %           initial guess gas hold up
```

```
HoverD=2;                                   %           ratio of the column height over
the column diameter
Dk=(Vr*4/(HoverD*pi))^(1/3);                %   [m]     Diameter kolom with H/D=2
Hk=HoverD*Dk;
Rk=Dk/2;                                    %   [m]     radius of the column
Ac=pi*Rk^2;                                 %   [m2]    cross sectional area of the
column
Acfree=Ac*0.6;                              %   [m2]    diameter available for liquid
and gas (no membranes)
db=3E-3;                                    %   [m]     diameter bubble
Aper=pi*(db^2)/4;                           %   [m2]    cross sectinal area of a bubble
Pxb=Pt+rho*g*Hk*(1-hldgem);                 %   [Pa]    Pressure at the bottom of the
column

% parameter to be optimalised
Fvg0=0.105;                                 %   [m3/s]  Air flow into the reactor

%Settings for the ODE solver:
x0=0;   xf = Hk;                            %   [m]     start and final integration
domain
Cga_0=yain.*(Pxb/(R*Tr)).*Mna;              %   [kg/m3] Initial gas phase
concentrations

% Integrated variables are put in VAR
VAR0=[Fvg0;Pxb;Cga_0];                      %   [-]     Initial conditions
xspan = [x0 xf];                            %           vector containing integration
domain
options = odeset('RelTol',1e-7,'AbsTol',1e-7);



%Call ODE solver:
[x,VARI] = ode45 ('deriv', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem); % call integration
procedure

%return essential data for further iteration
vgs=VARI(1:length(VARI),1)/Acfree;          %   [m/s]   superficial gas velocity
through the column
vg=0.25;                                    %   [m/s]   Actual gas velocity
hldgem0z=vgs/vg;                            %           Initial vector for iteration
containing the gas hold-up through the column
L0=x;                                       %   [m]     Rename column vector z to use
it in iteration
Hldgem=mean(hldgem0z);                      %           Averaged gas hold-up over the
column
Pxb=Pt+rho*g*Hk*(1-hldgem);                 %   [Pa]    Pressure at the bottom of the
column

%define matrix with average gas-hold ups for each iteration step

Gems=zeros(25,1);                           %           for each iteration a mean gas
hold-up is calculated and put in a vector
Pxbmatrix=zeros(25,1);                      %           Same for the bottem pressure

%iteration procedure

for i=1:25

    % Define initial conditions for each iteration step
    VAR0=[Fvg0;Pxb;Cga_0];

    %Call ODE solver:
    [x,VARI] = ode45 ('deriv2', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem0z,L0); % call integration
procedure

    % Return data for next iteration step
    vgs=VARI(1:length(VARI),1)/Ac;
    vg=0.25; %
    hldgem1z=vgs/vg;
    L1=x;
```

```
    hugems(i,1)=sum(hldgem1z)/length(L1);     %        Put the calculated mean hold-ups
in the initial vector
    hldgem0z=hldgem1z;                        %        Rename hold up profile for next
step
    L0=L1;                                    %        Rename column vector z to use it
in iteration
    Pxbmatrix(i,1)=Pt+rho*g*Hk*(1-hugems(i)); % [Pa]   Put the calculated bottem
pressure in the initial vector
    Pxb=Pxbmatrix(i);                         % [Pa]   Define new initial condition
end

%final average gas hold-up over last 10 iterations

hugemfin=mean(hugems((length(hugems)-10:length(hugems)),1));

%Calculate liquid volume
Vliq=Vr*(1-hlm)*(1-hugemfin);

%calculate gas volume
Vgas=Vr*(1-hlm)*hugemfin;

%the last one to give profiles with the calculated final mean values

[x,VARI] = ode45 ('deriv2', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem0z,L0); % call integration
procedure

% make variables workable
Fva_x=VARI(:,1);                %   [m3/s]  Air flow over the column
Cga=VARI(:,3:4);                %   [kg/m3] Concentration of the gases (air) over the
column
CgO2_x=VARI(:,3);               %   [kg/m3] Concetration of the O2 over the column
(air)
CgN2_x=VARI(:,4);               %   [kg/m3] Concetration of N2 over the column (air)
mtrO2_bubb=Fvg0*Cga_0-Fva_x(length(x))*[Cga(length(x),1:2)]'
MTO2req=MTR2a/3

disp('characteristics set by bubble column')
BC_Characteristics_Vliq_Vgas_gashld=[Vliq Vgas hugemfin]
mhu=npr/Ac

figure(5)
plot(x,Fva_x)

figure(6)
plot(x,Cga)


InAir_O2_N2=Fvg0*Cga_0              %   [kg/s]  Mass flow air into the column
Insyngas_H2_CO_CO2_N2=Fvsg0*Csg_0   %   [kg/s]  Mass flow synthesis gas into the column
Inbiomass=Fvliq*50                  %   [kg/s]  Mass flow residual biomass
InWater=Fvliq*(1000-50)             %   [kg/s]  Mass flow water into the reactor

UITair_O2_N2=Fva_x(length(x))*[Cga(length(x),1:2)]'
UITsyngas_H2_CO_CO2_N2=Fsvg_z(length(z))*VARM(length(z),1:4)'
UITbiomass=Fvliq*(1000-50)
UITPHB=150*Fvliq
UITCO2liq=ClgCO2fin*Fvliq


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%   CALCULATION OF THE ENERGY BALANCES  %%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%   Antoine Equation Parameters for water
%   log10(P) = A - (B / (T + C))
%   P = vapor pressure (bar)
%   T = temperature (K)
%   Temperature (K) A B C Reference Comment

A_B_C_H2O= [5.40221  1838.675  -31.737;         %  T= 273. - 303.
            5.20389  1733.926  -39.485 ;        %  T=304. - 333.
```

```
            5.07680  1659.793  -45.854;         %  T=334. - 363.
            5.08354  1663.125  -45.622;         %  T=-344. - 373.
            6.20963  2354.731    7.559] ;       %  T= 293. - 343.
%   Saturation Pressure water in the outlet stream

Aw=A_B_C_H2O(5,1); Bw=A_B_C_H2O(5,2); Cw=A_B_C_H2O(5,3);
Psatw = 10^(Aw - (Bw / (Tr + Cw)))
Pt_bar=Pt/101325                    %   [bar]   pressure on the top of the column
yvap_a_uit=Psatw/Pt_bar             %   [-]     Molar fraction vapour in the off air
gas


%   calculation of the air outlet composition (O2, N2, VAPOUR)
Flow_a_uit=Fva_x(length(x));            %   [m3/s]      volume flow of air over the
column
CgO2_mol_uit=CgO2_x(length(x))/Mna(1);  %   [mol/m3]    Molar concentration in Oxygen
over the column
CgN2_mol_uit=CgN2_x(length(x))/Mna(2);  %   [mol/m3]    Molar concentration

YO2=CgO2_mol_uit/(CgO2_mol_uit+CgN2_mol_uit)    %   [-] Molar fraction oxygen outlet
without vapour
YN2=CgN2_mol_uit/(CgO2_mol_uit+CgN2_mol_uit)    %   [-] Molar fraction nitrogen outlet
without vapour
yO2_vap=YO2/(1+yvap_a_uit)                      %   [-] Molar fraction oxygen outlet
with vapour
yN2_vap=YN2/(1+yvap_a_uit)                      %   [-] Molar fraction nitrogen outlet
with vapour
ya_uit=[yO2_vap;yN2_vap;yvap_a_uit]
yauit=ya_uit/sum(ya_uit)


%   Calculation of the synthesis gas outlet composition (H2, CO, CO2, N2)
Flow_sg_uit=Fsvg_z(length(z))/3;
CgH2sg_mol_uit=CgH2_z(length(z))/Mnsg(1);   %   [kg/m3] Outlet molar concentration
hydrogen
CgCOsg_mol_uit=CgCO_z(length(z))/Mnsg(2);   %   [kg/m3] Outlet molar concentration
carbon monoxide
CgCO2sg_mol_uit=CgCO2_z(length(z))/Mnsg(3); %   [kg/m3] Outlet molar concentration
carbon dioxide
CgN2sg_mol_uit=CgN2_z(length(z))/Mnsg(4);   %   [kg/m3] Outlet molar concentration
nitrogen
Cgsg_tot_uit=CgH2sg_mol_uit+CgCOsg_mol_uit+CgCO2sg_mol_uit+CgN2sg_mol_uit;
yH2sg_uit=CgH2sg_mol_uit/Cgsg_tot_uit;      %   [-] Molar fraction H2 outlet
yCOsg_uit=CgCOsg_mol_uit/Cgsg_tot_uit;      %   [-] Molar fraction CO outlet
yCO2sg_uit=CgCO2sg_mol_uit/Cgsg_tot_uit;    %   [-] Molar fraction CO2 outlet
yN2sg_uit=CgN2sg_mol_uit/Cgsg_tot_uit;      %   [-] Molar fraction N2 outlet
ysguit=[yH2sg_uit; yCOsg_uit; yCO2sg_uit; yN2sg_uit]


%   Molar masses of the streams coming in and out of the reactor


Msg_in=ysgin'*Mnsg          %  molar mass synthesis gas in
Ma_in=yain'*Mna             %  molar mass air in
Msg_uit=ysguit'*Mnsg        %  molar mass synthesis gas out
Ma_uit=yauit'*[Mna;Mw]      %  3 COMPONENTEN HEBBEN (O2, N2, H2O)!!!!!!

%   Densities of the streams coming in and out of the reactor
rhosg_in=Psg*Msg_in/(R*Tsg_in)      %   density of synthesis gas in
rhoa_in=Pxb*Ma_in/(R*Ta_in)         %   density of air in
rhosg_uit=Psg*Msg_uit/(R*Tr)        %   density of synthesis gas out
rhoa_uit=Pt*Ma_uit/(R*Tr)           %   density of air out (with water vapour)




%   DATA FOR THE CALCULATION OF THE HEAT CAPACITY OF SYNTHESIS GAS
%   THE DATA COMES FROM THE WEB SITE NIST
%      MATRIX=[   A;B;C;D;E;F;G;H ]
%                   H2          CO         CO2      N2
SG_H2_CO_CO2_N2= [33.066178    25.56759    24.99735    26.09200 ;
                 -11.363417    6.096130   55.18696    8.218801;
```

```
                 11.432816    4.054656  -33.69137  -1.976141;
                 -2.772874   -2.671301   7.948387   0.159274 ;
                 -0.158558    0.131021  -0.136638   0.044434 ;
                 -9.980797   -118.0089  -403.6075  -7.989230;
                172.707974   -110.5271   228.2431   221.0200;
                    0                0  -393.5224     0];

Enthrophy_H2_CO_CO2_N2=[ 130.680 ;197.660 ;213.785;  191.56] ;
Enthalphy_CO= -110.53;
Enthalphy_CO2=-393.51;

%   DATA FOR THE CALCULATION OF THE HEAT CAPACITY OF THE AIR
%    MATRIX=[   A;B;C;D;E;F;G;H ]
%            O2         N2
A_O2_N2=[29.65900 26.09200;
         6.137261  8.218801;
        -1.186521 -1.976141;
         0.095780  0.159274;
        -0.219663  0.044434;
        -9.861391 -7.989230;
         237.9480  221.0200;
         0.000000  0.000000];

S_O2_N2=[205.07; 191.56];  %    Entrophy of oxygen and nitrogen


%   Gaseous water or steam

DfH_H2O=241.826;          % [kJ/mol]    Enthalpy
S_H2O=188.835;            % [J/mol*K]   Entropy
Cp_vap=35;                % [J/mol*K]   Heat capacity

%   Liquid Water

DfH_W=-285.830 ;          % [kJ/mol]    Enthalpy
S_W=69.95  ;              % [J/mol*K]   Entropy

%     A        B           C           D           E        F          G           H
W=[-203.6060; 1523.290; -3196.413;  2474.455 ; 3.855326 ; -256.5478 ;-488.7163; -
285.8304];



%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%    HEAT CAPACITIES CALCULATION %%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%   INLET STREAMS: TEMPERATURES (Tsg_in, Ta_in, Tliq_in)
%   Heat capacity Synthesis gas
T=Tsg_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;                 %   Vector for the
calculation of the Heat capacities
Cp_H2_CO_CO2_N2=T_Cp'*SG_H2_CO_CO2_N2;                    %   [J/mol*K] heat capacity
per component syngas
Cpsg_in=ysgin'*Cp_H2_CO_CO2_N2'                           %   [J/mol*K] heat capacity
syngas in

%   Heat capacity Air
T=Ta_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cp_O2_N2=T_Cp'*A_O2_N2;                                   %   [J/mol*K] heat capacity
per component air
Cpa_in=yain'*Cp_O2_N2'                                    %   [J/mol*K] heat capacity
air in

%   Heat capacity of the broth
T=Tliq_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cpw_in=T_Cp'*W                                            %   [J/mol*K] heat capacity
water in
Cp_O2_N2_uit=[Cp_O2_N2 Cp_vap]
```

```
%   OUTLET STREAMS TEMPERATURE: Tr

T=Tr/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
%   Synthesis gas
Cp_H2_CO_CO2_N2_uit=T_Cp'*SG_H2_CO_CO2_N2;                   %   [J/mol*K] heat
capacity per component syngas
Cpsg_uit=ysguit'*Cp_H2_CO_CO2_N2_uit';                       %   [J/mol*K] heat
capacity syngas out

%   Air
Cp_O2_N2_uit=T_Cp'*A_O2_N2;
Cp_O2_N2_uit=[Cp_O2_N2_uit Cp_vap];                          %   [J/mol*K] heat
capacity per component air
Cpa_uit=yauit'*Cp_O2_N2_uit';                                %  [J/mol*K] heat capacity
air out

%   Broth
Cpw_uit=T_Cp'*W ;                                            %  [J/mol*K] heat capacity
water out (PHB neglected)


%   Evaporation enthalpy water
DHvapw=DfH_H2O-DfH_W;                                        %   [kJ/mol] Vaporization
Enthalpy

%   BALANCES
%   synthesis gas in
Fhsg_in=Fvsg0/3*rhosg_in*Cpsg_in*Tsg_in/(1000*Msg_in)        %   [kJ/s]
%   air in
Fha_in=Fvg0/3*rhoa_in*Cpa_in*Ta_in/(1000*Ma_in)              %   [kJ/s]
%   liquid out
Fhw_in=Fvliq*rho*Cpw_in*Tliq_in/(1000*Mw)                    %   [kJ/s]
%   synthesis gas out
Fhsg_uit=VARM(length(z),5)/3*rhosg_uit*Cpsg_uit*Tr/(1000*Msg_uit) %   [kJ/s]
%   air out
Fha_uit=VARI(length(x),1)*rhoa_uit*(Cpa_uit*Tr/(1000*Ma_uit)+yauit(3)*DHvapw/Mw) %
[kJ/s]
%   liquid out
Fhw_uit=Fvliq*rho*Cpw_uit*Tr/(1000*Mw)                       %   [kJ/s]
%   reaction heat
DHrH2=DfH_W
DHrCO=Enthalphy_CO2-Enthalphy_CO;
Rhr=mtH2*DHrH2/3+mtCO*DHrCO/3;

%   HEAT BALANS
Fhcooling=Fhsg_in+Fha_in+Fhw_in-Fhsg_uit-Fha_uit-Fhw_uit+Rhr;
%   Calculation of the heat exchanging area of the reactor (cooling-heating jacket)
UA=Fhcooling/(Tr-Tomgv)

%   Determining the cooling flow necessary

%   defining the dimensions of a dimple heat jacket see appendix mass & heat balances
Hjckt=1;                        %   Height of the jacket
d1=30e-3;                       %   dimensions dimples
d2=60e-3;                       %   dimensions dimples
Ajacket=pi*Dk*Hjckt;            %   Heat contacting surface area
U=-UA/Ajacket;                  %   Overall heat transfer coeficient
inU=1/U;

%   Heat conductivities
LmdaSSteel=16;                  %   [W/mK]  heat conductivity steel
lmdaW=0.596;                    %   [W/mK]  heat conductivity water

%   Heat conductivity inside wall of the reactor
Prbinnen=Cpw_uit*vis/lmdaW;                     %   [-]     Adimensional number Prandal
hbinnen=lmdaW/Dk*0.027*Re^0.8*Prbinnen^0.33;    %   [w/mK]   heat transfer coeficient
inside reactor

%   Heat conductivity of the wall of the reactor
Thickness_wall=7e-3;                            %   [m]     Thickness wall reactor
hwall=LmdaSSteel/Thickness_wall;                %   [W/mk]   heat transfer coeficient
```

```
wall material (steel)

%   Guess a cooling flow (water at 18 C)
Tcooling=5+273;                                 %   [K]     Temperature of the cooling
liquid

%   Heat conductivity of the jacket side
T=Tcooling/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cpcooling=T_Cp'*W ;
inhjacket=inU-(1/hwall+1/hbinnen);
hjacket=1/inhjacket;                            %   [W/mK]  heat transfer coeficient
Prjacket=Cpcooling*vis/lmdaW;                   %   [-]     Prandal number jacket
d0=(d1+d2)/2;                                   %   [m]     dimensions of the dimples
jRe=hjacket*d0/(lmdaW*Prjacket^(0.33));
x=0.075;                                        %   [m]     more dimensions of the
jacket (see appendix M&H balances)
w=x;                                            %   [m]

z=0.025;                                        %   [m]     dimensions of the jacket
(see appendix M&H balances)
Amin=z*(x-d0);                                  %   [m2]    minimal heat exchange area
Amax=z*x;                                       %   [m2]    maximal heat exchange area
Rejacket=(jRe/(0.0845*(w/x)^0.368*(Amin/Amax)^(-0.383)))^(1/0.695); %   [-]
Reynolds number in the cooling jacket
vmax=Rejacket*vis/(d0*rho);                     %   [m/s]   Velocity of the cooling
fluid in the jacket
ndimp=(Hjckt/w);                                %   [-]     Number of dimples
ndimples=ceil(ndimp);                           %   [-]     Rounded number of dimples
Fvdimple=vmax*Amin;                             %   [m3/s]  Flow cooling fluid per
dimple
Fvcooling=Fvdimple*ndimples                     %   [m3/s]  Total cooling fluid flow


%   Outputs of the file

%   concentrations of air and synthesis gas in the outlet of the reactor
Cg_a_tot_uit=CgO2_x(length(x))+CgN2_x(length(x))
Cgsg_tot_uit=(CgH2_z(length(z))+CgCO_z(length(z))+CgCO2_z(length(z))+CgN2_z(length(z)))

%   mass flows of the different streams comming in and out of the reactor
Fmsg_in=Fvsg0*rhosg_in;
Fma_in=Fvg0*rhoa_in;
Fmliq_in=Fvliq*rho;
Fmsg_uit=Flow_sg_uit*rhosg_uit;
Fma_uit=Flow_a_uit*rhoa_uit;
Fmliq_uit=Fmliq_in-Flow_a_uit*yvap_a_uit*Mw/Ma_uit+P_PHB;

%   Vector containing mass flows in and out
Fm_in=[Fmsg_in Fma_in Fmliq_in]
Fm_uit=[Fmsg_uit Fma_uit Fmliq_uit P_PHB]

%   Design variables, temperatures and presures
Tr_Pt_Psg_Tsg_in_Tliq_in_Ta_in_Tomgv=[Tr Pt Psg Tsg_in Tliq_in Ta_in Tomgv]
% Concentrations
Cp_H2_CO_CO2_N2_O2_N2=[Cp_H2_CO_CO2_N2 Cp_O2_N2]
```

```
%   Appendix 2-7-2: Stoichiometry of the PHB production phase


% This file deals with the production of PHB. In this file parameters concerning the
reactor (volume flows, volumes, concentrations, etc) which are
% set by the production rate and stoichiometrical balances are calculated. These
parameters are calculated and used to solve the
% Mass transfer rate determination according to the production of PHB.

function  Constraints=MBBM(Cxt,RAT)

% Data about the production of PHB known by constraints,
RP_PHB=1000*1000/(333*24*3600)  ;           % [kg/s] required production of PHB
DSP_loss=0.05      ;                        % [-] fraction of PHB lost in DSP
(initially assumed)
P_PHB=RP_PHB/(1-DSP_loss)   ;               % [kg/s] amount of PHB coming from second
reactor (R2)(=production in second reactor)
F_PHB=0.75   ;                              % [-]fraction PHB in the cells coming from
R2
Cxr=Cxt*(1-F_PHB)  ;                        % [kg/m3] concentration of residual Micr.
Biomass coming from R2
CPHB=Cxt*F_PHB ;                            % [kg/m3] concentration of PHB coming from
R2
PhiL=P_PHB/CPHB  ;                          % [m3/s] volume flow entering and leaving
R2

% Calculation of the stoichiometric constants of PHB production

StoichH2=25/((1/RAT)+1);                    % mol H2 / mol PHB
StoichCO=StoichH2/RAT  ;                    % mol CO / mol PHB
StoichO2=8;                                 % mol O2 / mol PHB
StoichH2O=StoichH2-3 ;                      % mol H2O / mol PHB
StoichCO2=StoichCO-4   ;                    % mol CO2/ mol PHB

% Yield of PHB production
YHPHB= StoichH2*(2/86) ;                    %   [kgi/kgPHB] i:H2, O2, CO, CO2, H2O
YCOPHB= StoichCO*(28/86) ;                  %   [kgi/kgPHB]
YCO2PHB= StoichCO2*(44/86);                 %   [kgi/kgPHB]
YH2OPHB=StoichH2O*(18/86) ;                 %   [kgi/kgPHB]
YOPHB=StoichO2*(16/86);

YiPHB=[YHPHB YCOPHB YCO2PHB YOPHB];


% Calculate the required transfer rates of H2 and CO and Oxigen and the
% produced or consumed amount of CO2

MTR2=(YiPHB)*RP_PHB;                      % [kg/s] required gas- liquid mass transfer
in inR2H

PhiL=[PhiL 0 0 0];
P_PHB=[P_PHB 0 0 0];

Constraints=[PhiL;MTR2;YiPHB;P_PHB];
```

```
%   Appendix 2-7-3: Desing of the growth reactor

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%      Fermentor calculations      %%
%%      Cpd3310 Production of PHB   %%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%   This file calculates the dimensions and operation characteristics of a
%   membrane bioreactor. It is divided in three sections: One for the
%   calculation of the required membrane surface to achieve the required
%   production of PHB. A second section where the dimensions of the reactor
%   are calculated accoording to the volume of the membranes, liquid and
%   gas bubbles.
%   Finally the energy balance is solved and the required cooling jacket
%   surface is calculated.

%   This file utilises 6 other files. 2 files for data of synthesis gas and
%   air gas. In this files permeabilities, diffusivities, etc are given. 1
%   file for the stoichiometric data of the reactions and 3 files
%   containing the mass balances, 2 of those are for the membrane surface
%   calculation and 1 for the reactor dimensions.


clear all               % clear variables in work space
format long e           % Floating point format with 15 digits.
clc                     % clear screen

%   CONSTANTS
g=9.81;                 %   [m2/s]      Gravity aceleration
R=8.3415;               %   [SI-units]  Gas constant
rho=1000;               %   [kg/m3]     density of broth
vis=0.001;              %   [kg/ms2]    viscosity of broth
Mw=18e-3;               %   [kg/mol]    Molecular weight of water

%   Conditions in the reactor and membranes
Tr=40+273;              %   [K]         Temperature of the reactor and gases
Psg=10*101325;          %   [Pa]        Pressure of the inlet synthesis gas
Pt=5*101325;            %   [Pa]        Pressure on the top of the reactor


Re=10000;               %   [-]         Reynolds number (from some table in the data
compainon)

% Inlet conditions
Tsg_in=40+273;           %   [K]     temperature of the synthesis gas into the reactor
Tliq_in=20+273;          %   [K]     temperature of the liquid
Ta_in=20+273;            %   [K]     temperature of the air (outside)
Tomgv=20+273;            %   [k]     temperature of the outside

% Composition of the synthesis gas in volume or molar fraction
yinH2=0.21;                                      %   [-]     Molar fraction H2 in
inflow
yinCO=0.17;                                      %   [-]     Molar fraction CO in
inflow
yinCO2=0.13;                                     %   [-]     molar fraction of CO2 in
inflow
yinN2=1-yinH2-yinCO-yinCO2;                     %   [-]     Molar fraction of N2 in
inflow
ysgin=[yinH2; yinCO; yinCO2; yinN2];             %   [-]     Vector containing the
molar fraction of SynGas

% Data on synthesis gas.

% For this the file Syg_Dat is
% called. This file has as inputs the temperature of the synthesis gas
% (equals the reaction temperature) the synthesis gas pressure and the
% viscosity of the liquid respectively. It return a matrix Sg_dat=[msg
% H Mnsg Perm DifL]. These are in respective order the dimensionless henry coefficient,
the
% henry coefficient in m3*Pa/mol, the molar mass, the permeability through the
% membranes and finally the liquid diffusities. The rows represent the
% substances, in respective order H2;CO;CO2.
```

```
SGConditions=[Tr; Psg;vis];                     %                  initiate input
vector (improvement compared to MBBM.m)
syn_data=Syg_Dat(SGConditions);                 %                  Call function file
msg=syn_data(:,1);                              %   [-]            dimensionless Henry
coefficient
H=syn_data(:,2);                                %   [m3*Pa/mol]    Henry coefficient
Mnsg=syn_data(:,3);                             %   [kg/mol]       molar mass
substances Syngas
Perm=syn_data(:,4);                             %   [mol/(s-m-Pa)] Permeability through
the membranes
DifL=syn_data(:,5);                             %   [m2/s]         Liquid diffusities

% Composition of air in gas volume or molar fraction
yinO2=0.21;                                    %   [-]     Molar fraction oxygen inflow
yinN2=1-yinO2;                                 %   [-]     Molar fraction of nitrogen
in inflow
yain=[yinO2; yinN2];                           %   [-]     Vector containing fraction
of the substances in air
Csg_0=ysgin.*(Psg/(R*Tr)).*Mnsg;               %   [kg/m3] Concentration of Nitrogen in
gas phase

%Synthesis gas flow rate
Fmsg0=3700/3600  ;                            % [kg/s]  Synthesis gas flowrate coming
from the reactor
Fmolsg0=Fmsg0/(ysgin'*Mnsg);                  % [mol/s] Synthesis gas flowrate coming
from the reactor
splitfact=1/4 ;                               %         Part of the delivered synthesis
gas going to the production reactor
Fvsg0=((Fmolsg0*splitfact)*R*Tr)/(Psg);       % [m3/s]  Air flow into the reactor

% Data on air.

% For this the file Ox_Dat is called. It does essentially the same as
% Syg_Dat. The inputs are the temperature in the reactor and the viscosity
% of the liquid respectively. It returns a matrix Oxg_dat=[ma Mna DifLa].
% These are in respective oreder the dimensionless henry coefficient, the
% molecular weight and the Liquid diffusities. The rows represent the
% substances, in respective order O2;N2.

OXConditions=[Tr;vis];                         %                Initiate input vector
Oxyg_data=Ox_Dat(OXConditions);                %                Call function file
ma=Oxyg_data(:,1);                             %    [-]         Henry coefficients
Mna=Oxyg_data(:,2);                            %    [kg/mol]    Molar mass
DifLa=Oxyg_data(:,3);                          %    [m2/s]      Diffusities

% Data on membranes

%   Data on membranes
%   the amount of membranes is a variable input!
Rmi=0.75e-3;                                   %   [m]     External radius of the
membranes
n=350000

;                                      %   [-]     number of membranes
thick=25e-6;                                   %   [m]     Thickness of a membrane
Rme=Rmi+thick;                                 %   [m]     Internal radius of the
membranes
hlm=0.25;                                       %   [-]     Space occupyed by the
membranes in the reactor
Rcyl=Rme*log(Rme/Rmi);                         %   [m]     Equivalent radius of the
membranes
Diam=2*Rme;                                    %   [m]     Averaged diameter of the
membranes

%   MEMBRANE MASS TRANSFER COEFICIENTS CALCULATIONS
Sc=vis./(DifL.*rho);                        %   [-]       Smidt number
Sh=1.45.*(Re.^0.32)*(Sc.^0.33);             %   [-]       Sherwood
klm=Sh.*DifL./(2.*Rme);                     %   [m/s]     Mass transfer coefficient
liquid on the membrane surface
km=Perm.*H./Rcyl;                           %   [m/s]     Mass transfer coefficient
```

```
membranes
k=1./((1./km)+(1./klm));                    %   [m/s]     Overall mass transfer
coefficient membranes




% start iteration procedure for finding minimum mebrane length
RAT=1.5;                                      %           initial consumed ratio
Lm=8;                                      %   [m]     initial Length of the single
membranes
differ_Lm=10;                               %           make sure iteration starts
precision=1                               %   [m]     precision of the iteration
(required min difference between
                                            %           given membrane length and best
guess value)
while differ_Lm>precision                   %   [m]     Persicion of the membrane
length calculation

    % Contraint DATA
    % Calling required mass transfer requirements by using the funtion file
    % MBBM. As input the file has a final concentration of the biomass with
    % PHB and a consumption ratio of H2 over CO. The file returns a matrix
    % called constraints=[PhiL;MTR1;YiPHB;P_PHB], With first column of Phil
    % is the liquid flowrate through the reactor and rest of the columns is
    % zero, MTR1 is the required consumed H2 CO CO2 and O2 (these are the
    % columns in respective order) for a given ratio, the yields of PHB on
    % the synthesis gas (H2, CO, CO2, O2 for the columns respectively) and
    % finally the required production of PHB with the last three columns
    % equal to zero

    Constraints=MBBMGR(50,RAT);                        %   Call funtion file for
constraints
    MTR1=Constraints(2,:);                            %   [kg/s]  REquired mass
transfer (H2 CO CO2 O2) to the production reactor
    Fvliq=Constraints(1,1);                               %   [m3/s]  Volumetric flow
stream
    MTR1sg=MTR1(1:3)';                                %   [kg/s]  Vector with the
required mass tranfer of SynGas [H2;CO;CO2]
    MTR1a=MTR1(4);                                    %   [kg/s]  Vector with the
required mass transfer of oxigen in air
    YiMB=Constraints(3,:);                           %   [kg/kg] Yield for PHB
production on H2 CO CO2 O2 respectivily
    P_xr=Constraints(4,1);                           %   [kg/s]  Expected PHB
production in the reactor

    % ODE solver settings
    options = odeset('RelTol',1e-4,'AbsTol',1e-4);    %     error tolerances of the
solver

    % Initial conditions for the solver
    % VARM is the vector containing the to be integrated variables.
    % [C_H2_0;C_CO_0;C_CO2_0;C_N2_0;Fv_0]
    z0=0;
    zf=Lm;
    zspan = [z0 zf];                            %   vector containing integration
domain
    VARM0=[Csg_0;Fvsg0];                        %   [-]     Initial conditions

    % Iteration procedure to find the liquid CO2 concentration at the given membrane
length

    % Iterative steps to calculate the liquid concentration of carbon dioxide. An
amount of
    % 'steps' values for the liquid  concentration are filled in starting at begin and
ending
    % at at begin+delta. For al steps the final liquid concentration is % calculated
with
    % Cl=(prod+trans)/Fvliq. The absolute least difference between the cl input and cl
calculated
    % is found and in the next iterative loop the filled in concentration starts at
```

```
value input
    % previous of the min cl difference and ends at the next. The loop stops when the
min
    % difference is smaller than error and finally returns the value of the
    % liquid concentration of carbon dioxide

    error=1e-4;                     % difference required between given liquid CO2
concentration and the calculated
    a=error+1;                       % initial difference to start procedure
    steps=100;                      % amount of points investigated per iteration
    begin=0.5;                      % initial first gues or beginning point of the
liquid CO2 concentration
    delta=10;                       % initial difference between the beginning liquid
concentration and the final one
    ClgCO2=zeros(steps,1);        % initiate vector containing the values of the
calculated liquid concentration

    while a>error ;
        for i=1:steps

            ClgCO2(i,1)=begin+(delta/(steps-1))*(i-1) ;     % vector containing given
liquid phase concentrations
            Clg=[0;0;ClgCO2(i)];                             % vectror containing all
liquid phase concentrations for the iteration

            %Call ODE solver:
            [z,VARM] = ode45 ('derimc', zspan, VARM0,
options,Diam,n,k,msg,R,Tr,Psg,Mnsg,Clg); % call integration procedure

            m_t_CO2=Fvsg0*Csg_0(3)-VARM(length(z),5)*VARM(length(z),3); % [kg/s]
amount of CO2 transfered
            m_t_CO=Fvsg0*Csg_0(2)-VARM(length(z),5)*VARM(length(z),2);  % [kg/s]
amount of CO transfer
            prodCO2=(m_t_CO/Mnsg(2)-P_xr/30e-3)*Mnsg(3);                % [kg/s]
amount of CO2 produced. NB 86e-3 is molar mass of PHB
            ClCO2calc(i,1)=(m_t_CO2+prodCO2)/Fvliq;                     % [kg/m3]
Caclulated liquid CO2 concentration


        end

        difference=abs(ClCO2calc-ClgCO2);       % calculate the absolute diffences
between the given and calculated liquid CO2 concentration
        [a b]=min(difference);                  % Find the minimum diffence and return
a the value and b the row number
        begin=ClgCO2(b-1);                      % give new beginning point for the
given CO2 concentrations. This points is the given point before the min difference
point
        delta=ClgCO2(b+1)-ClgCO2(b-1);          % state that the next run should end at
the point next to the min difference point

    end

    % Return the found values from the previous iteration procedure
    ClgCO2fin=ClgCO2(b)
    Clg=[0;0;ClgCO2fin];

    % Perform integration with found values to give answers
    [z,VARM] = ode45 ('derimc', zspan, VARM0, options,Diam,n,k,msg,R,Tr,Psg,Mnsg,Clg);
% call integration procedure

    % Transform answers in a workable form
    Fsvg_in=VARM(1,5);
    Fsvg_z=VARM(:,5);       %   [m3/s]        Flowrate through the membrane
    CgH2_z=VARM(:,1);       %   [kg/m3]       Concentration of hydrogen through the
membrane
    CgCO_z=VARM(:,2);       %   [kg/m3]       Concentration of CO through the membrane
    CgCO2_z=VARM(:,3);      %   [kg/m3]       Concentration of CO2 through the membrane
    CgN2_z=VARM(:,4);       %   [kg/m3]       Concentration of N2 through the membrane

    % calculate the mass transfer of H2 and CO through the column
    mtH2z=-Fsvg_z.*CgH2_z+Fvsg0*Csg_0(1);
```

```
    mtCOz=-Fsvg_z.*CgCO_z+Fvsg0*Csg_0(2);

    %calculate the final mass transefer
    mtH2=Fvsg0*Csg_0(1)-Fsvg_z(length(z),1)*CgH2_z(length(z))
    mtCO=Fvsg0*Csg_0(2)-Fsvg_z(length(z),1)*CgCO_z(length(z))
    mtCO2=Fvsg0*Csg_0(3)-Fsvg_z(length(z),1)*CgCO2_z(length(z));
    mtN2=Fvsg0*Csg_0(4)-Fsvg_z(length(z),1)*CgN2_z(length(z));

    % required mass transfer rates of H2 and CO
    mtH2req=MTR1sg(1)
    mtCOreq=MTR1sg(2)

    % Check if there is enough mass transfer. If  negative, not enough
    % mass transfer, if positive their is enough mass transfer
    SignH2=sign(mtH2-mtH2req);
    SignCO=sign(mtCO-mtCOreq);

    % Calculate the difference throught the column between the actual and
    % required mass transfer
    mtdifferH2z=mtH2z-mtH2req;
    mtdifferCOz=mtCOz-mtCOreq;

    % find the minimum difference between required and actual and return the row of z
at that difference
    [mtbestH2 zH2]=min(abs(mtdifferH2z));
    [mtbestCO zCO]=min(abs(mtdifferCOz));

    % Statements for next iteration cycle

    % If the there is not enough mass transfer enlong the membrane length
    % with 3 meters.
    if SignH2<0 | SignCO<0;
        Lmcalc=Lm
        Lm=Lm+3;                            % give new membrane length
        RAT=(mtH2*28)/(mtCO*2);             % give new best guess for the consumed
ratio (ratio at end of membrane)
        disp('not enough mass transfer');

    % If H2 is limiting
    elseif zH2>zCO;
        differ_Lm=Lm-z(zH2)                             % Calculate the diffence
between the given membrane length and the best gues
        Lmcalc=Lm                                       % Save the latest membrane
length
        Lm=Lm-precision/2;                              % If necessarry the next cycle
will use membranes 1 meter shorte
        [RowzNP]=find(z>(Lm-precision/2));              % Find the row in z for the
next membrane length
        RAT=(28*mtH2z(RowzNP(1)))/(2*mtCOz(RowzNP(1))); % Calculate the guess ratio for
the next given membrane length
        disp('H2 is limiting');

    % If CO is limiting
    else
        differ_Lm=Lm-z(zCO)
        Lmcalc=Lm
        Lm=Lm-precision/2;
        [RowzNP]=find(z>(Lm-precision/2));
        RAT=(28*mtH2z(RowzNP(1)))/(2*mtCOz(RowzNP(1)));
        disp('CO is limiting')
    end
end

% define losses of substrate.
loss=100*(Fsvg_z(length(z),1)*CgH2_z(length(z))+Fsvg_z(length(z),1)*CgCO_z(length(z)))/
((Fvsg0*Csg_0(1))+(Fvsg0*Csg_0(2)));
COloss=100*(Fsvg_z(length(z),1)*CgCO_z(length(z)))/(Fvsg0*Csg_0(2));

%   Membrane and reactor characteristics

Sm=2*pi*Rme*Lm*n;                       % [m2]      Total surface area of the membranes
Vm=pi*(Rme^2)*Lm*n;                     % [m3]      Volume of the membranes
```

```
Vr=Vm/hlm;                              % [m3]      Total reactor volume

disp('characteristics of the membrane bioreactor')
Dimensions_Sm_Vm_Vr=[Sm Vm Vr]

% Figures

figure(1);
plot(z,mtH2z,z,mtCOz);
title('mass transfer through the membrane');
xlabel('length of the membranes [m]');
ylabel('transfered gas [kg/s]');
legend('H2','CO');

figure(2)
plot(z,VARM(:,1:4));
title('concentrations of the gasses in the mebranes');
xlabel('length of the membranes [m]');
ylabel('concentration of gases [kg/m3]');
legend('H2','CO','CO2','N2');

figure(3)
plot(z,VARM(:,5));
title('volume flow rate through the membranes');
title('volume flow rate');
xlabel('length of the membrane [m]')
ylabel('volume flowrate [m3/s]')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%    calculation of the molar and mass fractions %%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%  SYNTHESIS GAS:  MOLAR FRACTIONS
CgH2sg_mol_z=CgH2_z./Mnsg(1);       %   [kg/m3] Concentration H2 over the length of the
membranes
CgCOsg_mol_z=CgCO_z./Mnsg(2);       %   [kg/m3] Concentration CO over the length of the
membranes
CgCO2sg_mol_z=CgCO2_z./Mnsg(3);     %   [kg/m3] Concentration CO2 over the length of
the membranes
CgN2sg_mol_z=CgN2_z./Mnsg(4);       %   [kg/m3] Concentration N2 over the length of the
membranes
Cgsg_tot_z=CgH2sg_mol_z+CgCOsg_mol_z+CgCO2sg_mol_z+CgN2sg_mol_z;
yH2_mol_z=CgH2sg_mol_z./Cgsg_tot_z;     %   [-] H2
yCO_mol_z=CgCOsg_mol_z./Cgsg_tot_z;     %   [-] CO
yCO2_mol_z=CgCO2sg_mol_z./Cgsg_tot_z;   %   [-] CO2
yN2_mol_z=CgN2sg_mol_z./Cgsg_tot_z;     %   [-] N2
ysg_mol_z=[yH2_mol_z yCO_mol_z yCO2_mol_z yN2_mol_z];

mtH2zmol=-Fsvg_z.*CgH2sg_mol_z+Fvsg0*Csg_0(1);
mtCOzmol=-Fsvg_z.*CgCOsg_mol_z+Fvsg0*Csg_0(2);


figure(4); plot(z,yH2_mol_z,z,yCO_mol_z,z,yCO2_mol_z,z,yN2_mol_z);
title('Molar fraction of gases in the mebrane');
xlabel('length of the membranes [m]');
ylabel('molar fraction of gases in the membranes [kg/m3]');
legend('H2','CO','CO2','N2');




%   Characteristics for the bubble column
hldgem=0.2;                                 %           initial guess gas hold up
HoverD=2.3;                                 %           ratio of the column height over
the column diameter
Dk=(Vr*4/(HoverD*pi))^(1/3);                %   [m]     Diameter kolom with H/D=2
Hk=HoverD*Dk;
Rk=Dk/2;                                    %   [m]     radius of the column
Ac=pi*Rk^2;                                 %   [m2]    cross sectional area of the
column
Acfree=Ac*hlm;                              %   [m2]    diameter available for liquid
and gas (no membranes)
db=3E-3;                                    %   [m]     diameter bubble
```

```
Aper=pi*(db^2)/4;                           %   [m2]    cross sectinal area of a bubble
Pxb=Pt+rho*g*Hk*(1-hldgem);                 %   [Pa]    Pressure at the bottom of the
column

% parameter to be optimalised
Fvg0=0.142;                                 %   [m3/s]  Air flow into the reactor

%Settings for the ODE solver:
x0=0;   xf = Hk;                            %   [m]     start and final integration
domain
Cga_0=yain.*(Pxb/(R*Tr)).*Mna;              %   [kg/m3] Initial gas phase
concentrations

% Integrated variables are put in VAR
VAR0=[Fvg0;Pxb;Cga_0];                      %   [-]     Initial conditions
xspan = [x0 xf];                            %           vector containing integration
domain
options = odeset('RelTol',1e-7,'AbsTol',1e-7);



%Call ODE solver:
[x,VARI] = ode45 ('deriv', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem); % call integration
procedure

%return essential data for further iteration
vgs=VARI(1:length(VARI),1)/Acfree;          %   [m/s]   superficial gas velocity
through the column
vg=0.2;                                     %   [m/s]   Actual gas velocity
hldgem0z=vgs/vg;                            %           Initial vector for iteration
containing the gas hold-up through the column
L0=x;                                       %   [m]     Rename column vector z to use
it in iteration
Hldgem=mean(hldgem0z);                      %           Averaged gas hold-up over the
column
Pxb=Pt+rho*g*Hk*(1-hldgem);                 %   [Pa]    Pressure at the bottom of the
column

%define matrix with average gas-hold ups for each iteration step

Gems=zeros(25,1);                           %           for each iteration a mean gas
hold-up is calculated and put in a vector
Pxbmatrix=zeros(25,1);                      %           Same for the bottem pressure

%iteration procedure

for i=1:25

    % Define initial conditions for each iteration step
    VAR0=[Fvg0;Pxb;Cga_0];

    %Call ODE solver:
    [x,VARI] = ode45 ('deriv2', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem0z,L0); % call integration
procedure

    % Return data for next iteration step
    vgs=VARI(1:length(VARI),1)/Ac;
    vg=0.2; %
    hldgem1z=vgs/vg;
    L1=x;
    hugems(i,1)=sum(hldgem1z)/length(L1);     %        Put the calculated mean hold-ups
in the initial vector
    hldgem0z=hldgem1z;                        %        Rename hold up profile for next
step
    L0=L1;                                    %        Rename column vector z to use it
in iteration
    Pxbmatrix(i,1)=Pt+rho*g*Hk*(1-hugems(i)); % [Pa]   Put the calculated bottem
pressure in the initial vector
    Pxb=Pxbmatrix(i);                         % [Pa]   Define new initial condition
end
```

```
%final average gas hold-up over last 10 iterations

hugemfin=mean(hugems((length(hugems)-10:length(hugems)),1));

%Calculate liquid volume
Vliq=Vr*(1-hlm)*(1-hugemfin);

%calculate gas volume
Vgas=Vr*(1-hlm)*hugemfin;

%the last one to give profiles with the calculated final mean values

[x,VARI] = ode45 ('deriv2', xspan, VAR0,
options,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem0z,L0); % call integration
procedure

% make variables workable
Fva_x=VARI(:,1);            %   [m3/s]  Air flow over the column
Cga=VARI(:,3:4);            %   [kg/m3] Concentration of the gases (air) over the
column
CgO2_x=VARI(:,3);           %   [kg/m3] Concetration of the O2 over the column (air)
CgN2_x=VARI(:,4);           %   [kg/m3] Concetration of N2 over the column (air)
mtrO2_bubb=Fvg0*Cga_0-Fva_x(length(x))*[Cga(length(x),1:2)]'
MTO2req=MTR1a

disp('characteristics set by bubble column')
BC_Characteristics_Vliq_Vgas_gashld=[Vliq Vgas hugemfin]


figure(5);
plot(x,Fva_x);

figure(6);
plot(x,Cga);


InAir_O2_N2=Fvg0*Cga_0              %   [kg/s]  Mass flow air into the column
Insyngas_H2_CO_CO2_N2=Fvsg0*Csg_0   %   [kg/s]  Mass flow synthesis gas into the column
InWater=Fvliq*1000                  %   [kg/s]  Mass flow water into the reactor

UITair_O2_N2=Fva_x(length(x))*[Cga(length(x),1:2)]'
UITsyngas_H2_CO_CO2_N2=Fsvg_z(length(z))*VARM(length(z),1:4)'
UITbiomass=Fvliq*50
UITCO2liq=ClgCO2fin*Fvliq


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%   CALCULATION OF THE ENERGY BALANCES  %%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%   Antoine Equation Parameters for water
%   log10(P) = A - (B / (T + C))
%   P = vapor pressure (bar)
%   T = temperature (K)
%   Temperature (K) A B C Reference Comment

A_B_C_H2O= [5.40221  1838.675  -31.737;         %  T= 273. - 303.
            5.20389  1733.926  -39.485 ;        %  T=304. - 333.
            5.07680  1659.793  -45.854;         %  T=334. - 363.
            5.08354  1663.125  -45.622;         %  T=-344. - 373.
            6.20963  2354.731    7.559] ;       %  T= 293. - 343.
%   Saturation Pressure water in the outlet stream

Aw=A_B_C_H2O(5,1); Bw=A_B_C_H2O(5,2); Cw=A_B_C_H2O(5,3);
Psatw = 10^(Aw - (Bw / (Tr + Cw)));
Pt_bar=Pt/101325;                           %   [bar]   pressure on the top of the
column
yvap_a_uit=Psatw/Pt_bar;                    %   [-]     Molar fraction vapour in the
off air gas

%   calculation of the air outlet composition (O2, N2, VAPOUR)
```

```
Flow_a_uit=Fva_x(length(x));                % [m3/s]      volume flow of air over the
column
CgO2_mol_uit=CgO2_x(length(x))/Mna(1);      % [mol/m3]    Molar concentration in
Oxygen over the column
CgN2_mol_uit=CgN2_x(length(x))/Mna(2);      % [mol/m3]    Molar concentration

YO2=CgO2_mol_uit/(CgO2_mol_uit+CgN2_mol_uit);   %   [-] Molar fraction oxygen outlet
without vapour
YN2=CgN2_mol_uit/(CgO2_mol_uit+CgN2_mol_uit);   %   [-] Molar fraction nitrogen outlet
without vapour
yO2_vap=YO2/(1+yvap_a_uit);                     %   [-] Molar fraction oxygen outlet
with vapour
yN2_vap=YN2/(1+yvap_a_uit);                     %   [-] Molar fraction nitrogen outlet
with vapour
ya_uit=[yO2_vap;yN2_vap;yvap_a_uit];
yauit=ya_uit/sum(ya_uit);


%   Calculation of the synthesis gas outlet composition (H2, CO, CO2, N2)
Flow_sg_uit=Fsvg_z(length(z))/3;
CgH2sg_mol_uit=CgH2_z(length(z))/Mnsg(1);       %   [kg/m3] Outlet molar concentration
hydrogen
CgCOsg_mol_uit=CgCO_z(length(z))/Mnsg(2);       %   [kg/m3] Outlet molar concentration
carbon monoxide
CgCO2sg_mol_uit=CgCO2_z(length(z))/Mnsg(3);     %   [kg/m3] Outlet molar concentration
carbon dioxide
CgN2sg_mol_uit=CgN2_z(length(z))/Mnsg(4);       %   [kg/m3] Outlet molar concentration
nitrogen
Cgsg_tot_uit=CgH2sg_mol_uit+CgCOsg_mol_uit+CgCO2sg_mol_uit+CgN2sg_mol_uit;
yH2sg_uit=CgH2sg_mol_uit/Cgsg_tot_uit;          %   [-] Molar fraction H2 outlet
yCOsg_uit=CgCOsg_mol_uit/Cgsg_tot_uit;          %   [-] Molar fraction CO outlet
yCO2sg_uit=CgCO2sg_mol_uit/Cgsg_tot_uit;        %   [-] Molar fraction CO2 outlet
yN2sg_uit=CgN2sg_mol_uit/Cgsg_tot_uit;          %   [-] Molar fraction N2 outlet
ysguit=[yH2sg_uit; yCOsg_uit; yCO2sg_uit; yN2sg_uit]


%   Molar masses of the streams coming in and out of the reactor


Msg_in=ysgin'*Mnsg       ;   %  molar mass synthesis gas in
Ma_in=yain'*Mna         ;    %  molar mass air in
Msg_uit=ysguit'*Mnsg     ;   %  molar mass synthesis gas out
Ma_uit=yauit'*[Mna;Mw]    ;  %  3 COMPONENTEN HEBBEN (O2, N2, H2O)!!!!!!

%   Densities of the streams coming in and out of the reactor
rhosg_in=Psg*Msg_in/(R*Tsg_in);      %   density of synthesis gas in
rhoa_in=Pxb*Ma_in/(R*Ta_in)   ;      %   density of air in
rhosg_uit=Psg*Msg_uit/(R*Tr)   ;     %   density of synthesis gas out
rhoa_uit=Pt*Ma_uit/(R*Tr)      ;     %   density of air out (with water vapour)




%   DATA FOR THE CALCULATION OF THE HEAT CAPACITY OF SYNTHESIS GAS
%   THE DATA COMES FROM THE WEB SITE NIST
%      MATRIX=[   A;B;C;D;E;F;G;H ]
%                  H2          CO          CO2      N2
SG_H2_CO_CO2_N2= [33.066178    25.56759    24.99735    26.09200 ;
                 -11.363417    6.096130    55.18696    8.218801;
                  11.432816    4.054656  -33.69137   -1.976141;
                  -2.772874   -2.671301    7.948387   0.159274 ;
                  -0.158558    0.131021  -0.136638    0.044434 ;
                  -9.980797   -118.0089  -403.6075   -7.989230;
                 172.707974   -110.5271   228.2431    221.0200;
                      0               0  -393.5224       0];

Enthrophy_H2_CO_CO2_N2=[ 130.680 ;197.660 ;213.785;  191.56] ;
Enthalphy_CO= -110.53;
Enthalphy_CO2=-393.51;

%   DATA FOR THE CALCULATION OF THE HEAT CAPACITY OF THE AIR
%    MATRIX=[   A;B;C;D;E;F;G;H ]
```

```
%            O2         N2
A_O2_N2=[29.65900 26.09200;
         6.137261  8.218801;
        -1.186521 -1.976141;
         0.095780  0.159274;
        -0.219663  0.044434;
        -9.861391 -7.989230;
         237.9480  221.0200;
         0.000000  0.000000];

S_O2_N2=[205.07; 191.56];  %    Entrophy of oxygen and nitrogen


%   Gaseous water or steam

DfH_H2O=241.826;           % [kJ/mol]    Enthalpy
S_H2O=188.835;             % [J/mol*K]   Entropy
Cp_vap=35;                 % [J/mol*K]   Heat capacity

%   Liquid Water

DfH_W=-285.830 ;           % [kJ/mol]    Enthalpy
S_W=69.95  ;               % [J/mol*K]   Entropy


%     A        B           C           D           E        F          G           H
W=[-203.6060; 1523.290; -3196.413;  2474.455 ; 3.855326 ; -256.5478 ;-488.7163; -
285.8304];



%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%    HEAT CAPACITIES CALCULATION %%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%   INLET STREAMS: TEMPERATURES (Tsg_in, Ta_in, Tliq_in)
%   Heat capacity Synthesis gas

                  %[J/mol*K]

T=Tsg_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;                        %   Vector for the
calculation of the Heat capacities
Cp_H2_CO_CO2_N2=T_Cp'*SG_H2_CO_CO2_N2;                           %   [J/mol*K] heat capacity
per component syngas
Cpsg_in=ysgin'*Cp_H2_CO_CO2_N2'                                  %   [J/mol*K] heat capacity
syngas in

%   Heat capacity Air
T=Ta_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cp_O2_N2=T_Cp'*A_O2_N2;                                          %   [J/mol*K] heat capacity
per component air
Cpa_in=yain'*Cp_O2_N2'                                           %   [J/mol*K] heat capacity
air in

%   Heat capacity of the broth
T=Tliq_in/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cpw_in=T_Cp'*W                                                   %   [J/mol*K] heat capacity
water in
Cp_O2_N2_uit=[Cp_O2_N2 Cp_vap]

%   OUTLET STREAMS TEMPERATURE: Tr

T=Tr/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
%   Synthesis gas
Cp_H2_CO_CO2_N2_uit=T_Cp'*SG_H2_CO_CO2_N2;                        %   [J/mol*K] heat
capacity per component syngas
Cpsg_uit=ysguit'*Cp_H2_CO_CO2_N2_uit';                            %   [J/mol*K] heat
capacity syngas out
```

```
%   Air
Cp_O2_N2_uit=T_Cp'*A_O2_N2;
Cp_O2_N2_uit=[Cp_O2_N2_uit Cp_vap];                          %   [J/mol*K] heat
capacity per component air
Cpa_uit=yauit'*Cp_O2_N2_uit';                                %  [J/mol*K] heat capacity
air out

%   Broth
Cpw_uit=T_Cp'*W ;                                            %  [J/mol*K] heat capacity
water out (PHB neglected)


%   Evaporation enthalpy water
DHvapw=DfH_H2O-DfH_W;                                        %   [kJ/mol] Vaporization
Enthalpy

%   BALANCES
%   synthesis gas in
Fhsg_in=Fvsg0*rhosg_in*Cpsg_in*Tsg_in/(1000*Msg_in)    ;                %[kJ/s]
%   air in
Fha_in=Fvg0*rhoa_in*Cpa_in*Ta_in/(1000*Ma_in);
%   liquid out
Fhw_in=Fvliq*rho*Cpw_in*Tliq_in/(1000*Mw);
%   synthesis gas out
Fhsg_uit=VARM(length(z),5)*rhosg_uit*Cpsg_uit*Tr/(1000*Msg_uit);
%   air out
Fha_uit=VARI(length(x),1)*rhoa_uit*(Cpa_uit*Tr/(1000*Ma_uit)+yauit(3)*DHvapw/Mw);
%   liquid out
Fhw_uit=Fvliq*rho*Cpw_uit*Tr/(1000*Mw);
%   reaction heat
DHrH2=DfH_W;
DHrCO=Enthalphy_CO2-Enthalphy_CO;
Rhr=mtH2*DHrH2+mtCO*DHrCO;

%   HEAT BALANS
Fhcooling=Fhsg_in+Fha_in+Fhw_in-Fhsg_uit-Fha_uit-Fhw_uit+Rhr;
%   Calculation of the heat exchanging area of the reactor (cooling-heating jacket)
UA=Fhcooling/(Tr-Tomgv);

%   defining the dimensions of a dimple heat jacket see appendix mass & heat balances
Hjckt=1;                        %   Height of the jacket
d1=30e-3;                       %   dimensions dimples
d2=60e-3;                       %   dimensions dimples
Ajacket=pi*Dk*Hjckt;            %   Heat contacting surface area
U=-UA/Ajacket;                  %   Overall heat transfer coeficient
inU=1/U;

%   Heat conductivities
LmdaSSteel=16;                  %   [W/mK]  heat conductivity steel
lmdaW=0.596;                    %   [W/mK]  heat conductivity water

%   Heat conductivity inside wall of the reactor
Prbinnen=Cpw_uit*vis/lmdaW;                     %   [-]     Adimensional number Prandal
hbinnen=lmdaW/Dk*0.027*Re^0.8*Prbinnen^0.33;    %   [w/mK]   heat transfer coeficient
inside reactor

%   Heat conductivity of the wall of the reactor
Thickness_wall=7e-3;                            %   [m]     Thickness wall reactor
hwall=LmdaSSteel/Thickness_wall;                %   [W/mk]   heat transfer coeficient
wall material (steel)

%   Guess a cooling flow (water at 18 C)
Tcooling=5+273;                                 %   [K]     Temperature of the cooling
liquid

%   Heat conductivity of the jacket side
T=Tcooling/1000;
T_Cp=[1; T; T^2; (T^3); 1/T^2; 0; 0; 0] ;
Cpcooling=T_Cp'*W ;
inhjacket=inU-(1/hwall+1/hbinnen);
hjacket=1/inhjacket;                            %   [W/mK]  heat transfer coeficient
Prjacket=Cpcooling*vis/lmdaW;                   %   [-]     Prandal number jacket
```

```
d0=(d1+d2)/2;                                      %   [m]     dimensions of the dimples
jRe=hjacket*d0/(lmdaW*Prjacket^(0.33));
x=0.075;                                           %   [m]     more dimensions of the
jacket (see appendix M&H balances)
w=x;                                               %   [m]

z=0.025;                                           %   [m]     dimensions of the jacket
(see appendix M&H balances)
Amin=z*(x-d0);                                     %   [m2]    minimal heat exchange area
Amax=z*x;                                          %   [m2]    maximal heat exchange area
Rejacket=(jRe/(0.0845*(w/x)^0.368*(Amin/Amax)^(-0.383)))^(1/0.695); %   [-]
Reynolds number in the cooling jacket
vmax=Rejacket*vis/(d0*rho);                        %   [m/s]   Velocity of the cooling
fluid in the jacket
ndimp=(Hjckt/w);                                   %   [-]     Number of dimples
ndimples=ceil(ndimp);                              %   [-]     Rounded number of dimples
Fvdimple=vmax*Amin;                                %   [m3/s]  Flow cooling fluid per
dimple
Fvcooling=Fvdimple*ndimples                        %   [m3/s]  Total cooling fluid flow

%   Outputs of the file
Cg_a_tot_uit=CgO2_x(length(x))+CgN2_x(length(x));
Cgsg_tot_uit=(CgH2_z(length(z))+CgCO_z(length(z))+CgCO2_z(length(z))+CgN2_z(length
(z)));

Fmsg_in=Fvsg0*rhosg_in;
Fma_in=Fvg0*rhoa_in;
Fmliq_in=Fvliq*rho;
Fmsg_uit=Flow_sg_uit*rhosg_uit;
Fma_uit=Flow_a_uit*rhoa_uit;
Fmliq_uit=Fmliq_in-Flow_a_uit*yvap_a_uit*Mw/Ma_uit+P_xr;;

Fm_in=[Fmsg_in Fma_in Fmliq_in]
Fm_uit=[Fmsg_uit Fma_uit Fmliq_uit P_xr]
```

```
%   Appendix 2-7-4: Stoichiometry of the Residual biomass production phase

% This file deals with the microbial biomass side of both the fermenters (continues
inoculum reactor and the continues
% PHB production reactor). In this file parameters concerning the reactor (volume
flows, volumes, concentrations, etc) which are
% set by the production rate and stoichiometrical balances are calculated. These
parameters are calculated and used to solve the
% Mass transfer rate determination according to the production of PHB.
function  Constraints=MBBM(Cxt,RAT)

% Data about the production of PHB known by constraints,
RP_PHB=1000*1000/(333*24*3600)  ;           % [kg/s] required production of PHB
DSP_loss=0.05      ;                        % [-] fraction of PHB lost in DSP
(initially assumed)
P_PHB=RP_PHB/(1-DSP_loss)   ;               % [kg/s] amount of PHB coming from second
reactor (R2)(=production in second reactor)
F_PHB=0.75   ;                              % [-]fraction PHB in the cells coming from
R2
Cxr=Cxt*(1-F_PHB)  ;                        % [kg/m3] concentration of residual Micr.
Biomass coming from R2
CPHB=Cxt*F_PHB ;                            % [kg/m3] concentration of PHB coming from
R2
PhiL=P_PHB/CPHB  ;                          % [m3/s] volume flow entering and leaving
R2
PhiR1=PhiL*Cxr/Cxt;                         % [m3/s] volume flow rate entering and
leaving rhe growth reactor
P_xr=PhiL*Cxr;                              % [kg/s] required residual biomass
production

%yields for growth,
StoichH2BM=6/((1/RAT)+1);                  % mol H2 / mol PHB
StoichCOBM=StoichH2BM/RAT  ;               % mol CO / mol PHB
StoichO2BM=2;                              % mol O2 / mol PHB
StoichH2OBM=StoichH2BM-1 ;                 % mol H2O / mol PHB
StoichCO2BM=StoichCOBM-1   ;               % mol CO2/ mol PHB

YHBM= StoichH2BM*(2/30) ;                %   [kgi/kgx] i:H2, O2, CO, CO2, H2O
YCOBM= StoichCOBM*(28/30) ;              %   [kgi/kgx]
YCO2BM= StoichCO2BM*(44/30);             %   [kgi/kgx]
YH2OBM=StoichH2OBM*(18/30) ;             %   [kgi/kgx]
YOBM=StoichO2BM*(32/30);

YiBM=[YHBM YCOBM YCO2BM YOBM];


% Calculate the required transfer rates of H2 and CO and Oxigen and the
% produced or consumed amount of CO2

MTR1=(YiBM)*P_xr;                      % [kg/s] required gas- liquid mass transfer in
inR2H

PhiR1=[PhiR1 0 0 0];
P_xr=[P_xr 0 0 0];

Constraints=[PhiR1;MTR1;YiBM;P_xr];
```

```
%   Appendix 2-7-5: Data of the syn-gas

%   Input variables for the membrane bioreactor SYNTHESIS GAS

function Sg_dat=Syg_Dat(SGConditions)

%   COMPOSITION INFLOW GAS

Tr=SGConditions(1);
Psg=SGConditions(2);
vis=SGConditions(3);

%henry constants

% Matrix containing the value of the dimensionless henry constant at different
temperatures. Rows are components[H2;CO;CO2]
% Columns are temperature [283;293;303;313;323;333]
mT=[46.98   50.45 53.84 55.47 63.89 56.5;
    32.65   39.59 45.79 51.41 56.21 60.64;
   0.7682   1.049 1.374 1.721 2.09  2.519;
    49.34   59.38 68.25 76.82 83.46 88.63];

% Linear interpolation between the henry constants at given temperature

if Tr<283
    disp('no data for the henry constant exists at this temperature');
    return
elseif Tr<293
     m=((mT(:,2)-mT(:,1))./10).*(Tr-283)+mT(:,1);
 elseif Tr<303
       m=((mT(:,3)-mT(:,2))./10).*(Tr-293)+mT(:,2);
   elseif Tr<313
         m=((mT(:,4)-mT(:,3))./10).*(Tr-303)+mT(:,3);
     elseif Tr<323
          m=((mT(:,5)-mT(:,4))./10).*(Tr-313)+mT(:,4);
      elseif Tr<333
             m=((mT(:,6)-mT(:,5))./10).*(Tr-323)+mT(:,5);
         else
             return
             disp('no data for the henry constant exists at this temperature');

end

msg=m;

% Matrix containing the value of the henry constant in [m3*Pa/mol] at different
temperature.  Rows are components[H2;CO;CO2]
% Columns are temperature [283;293;303;313;323;333]

HT=[116400  125000   133500   137500   158400   140100;
    80930   98140 113500   127400   139300   150300;
    1904 2600  3405  4266  5181  6243;
    122300  147200   169200   190400   206900   219700];

if Tr<283
    disp('no data for the henry constant exists at this temperature')
    return
elseif Tr<293
     H=((HT(:,2)-HT(:,1))./10).*(Tr-283)+HT(:,1);
 elseif Tr<303
       H=((HT(:,3)-HT(:,2))./10).*(Tr-293)+HT(:,2);
   elseif Tr<313
         H=((HT(:,4)-HT(:,3))./10).*(Tr-303)+HT(:,3);
     elseif Tr<323
          H=((HT(:,5)-HT(:,4))./10).*(Tr-313)+HT(:,4);
      elseif Tr<333
             H=((HT(:,6)-HT(:,5))./10).*(Tr-323)+HT(:,5);
         else
             return
             disp('no data for the henry constant exists at this temperature');

end
```

```
%   MOLECULAR MASSES
MH2=2e-3;                                         %   [kg/mol]     Molecular mass
hydrogen
MCO=28e-3;                                        %   [kg/mol]     Molecular mass
carbon monoxide
MCO2=44e-3;                                       %   [kg/mol]     Molecular mass
carbon dioxide
MN2=28e-3;

Mnsg=[MH2;MCO;MCO2;MN2];



%   DIFFUSION THROUGH SILICONE RUBBER MEMBRANE [permeability=diffusion*Area]
literature:Christie John Geankoplis
f=3.1087e-6;                                %   [units=>SI units]   Conversion factor
for permeabilities
PermH2=550E-10*f;                           %   [mol/(s-m-Pa)]      Permeability of
hydrogen trough silicone rubber [20C]
PermCO2=2700E-10*f;                         %   [mol/(s-m-Pa)]      Permeability of
Carbon monoxide trough silicone rubber [20C]
PermCO=550E-10*f;                           %   [mol/(s-m-Pa)]      Permeability of
Carbon dioxide trough silicone rubber  [20C]
PermN2=0.00000000001;

% permeability CO=30 N2=25 moeten nog met factor vermenigvuldigd worden

Perm=[PermH2;PermCO;PermCO2;PermN2];


%   DIFFUSION THROUGH LIQUID (WATER)
% Diffusion of gases through water. Water diffusities are not widely available for each
gaseous substance, especially not at different
% temperatures. For this reason different models are used for the different substances.
For H2 and CO2 linear relation were derived
% from experimental data (Handbook of Chemistry and Physics, 84th edition), this seems
a good assumption since it is a small temperature
% range and the least squar sum is in all cases higer than 0.99. For Carbon monoxide no
data is available  so for this reason
% the Wilke and chang relation for diffusion wil be used (Coulson and richardson deel 1
blz 597). This relation will also be used for
% nitrogen. Data on diffusion of nitrogen in water only available at 25 degrees celcius
and the Wilke and Chang relation gives good
% approximation for the diffusion coefficient of nitrogen at 25 degrees. The
temperature range starts at 283 degrees kelvin and ends at
% 333. Not is this only a safe range but the files quits otherwise at the calculation
of the henry constants.

VaCO=0.0307;                                            % [m3/kmol] diffusion volume
of CO (Coulson and richardson deel 1 blz 585)
VaN2=0.0312;                                            % [m3/kmol] diffusion volume
of N2 (coulson and richardson deel 1 blz 585)

DifLH2=1.074857143E-10*(Tr-273) + 2.479904762E-09;   % [m2/s] linear relato\ion derived
from experimental data for the diffusion
                                                       % of H2 in water. R2 =
9.970475060E-01
DifLCO=(1.173e-16*2.26^0.5*18^0.5*Tr)/(vis*VaCO^0.6);   % [m2/s] relation for diffusion
coefficient of CO. 2.26 is the association factor of the
                                                       % solvent in this case water
and 18 is the molecular weight of the solvent.
DifLCO2=4.291428571E-11*(Tr-273) + 8.094285714E-10  ;     % [m2/s] linear relato\ion
derived from experimental data for the diffusion
                                                       % of CO2 in water. R2 =
9.950178627E-01
DifLN2=(1.173e-16*2.26^0.5*18^0.5*Tr)/(vis*VaN2^0.6);   % [m2/s] relation for diffusion
coefficient N2. 2.26 is the association factor of the
                                                       % solvent in this case water
and 18 is the molecular weight of the solvent.
```

```
DifL=[DifLH2;DifLCO;DifLCO2;DifLN2];


DifL=[DifLH2;DifLCO;DifLCO2;DifLN2];

%   Output data
Sg_dat=[msg H Mnsg Perm DifL];
```

```
%   Appendix 2-7-6: Data of the air

%   Input variables for the membrane bioreactor OXYGEN (AIR)


function Oxg_dat=Ox_Dat(OXConditions)


%   COMPOSITION INFLOW GAS

Tr=OXConditions(1);
vis=OXConditions(2);



%   HENRY CONSTANTS (T=20C)

mT=[24.15   29.62 35.08 39.52 43.43 46.46;
    49.34   59.38 68.25 76.82 83.46 88.63];

if Tr<283
    disp('no data for the henry constant exists at this temperature');
    return
elseif Tr<293
     m=((mT(:,2)-mT(:,1))./10).*(Tr-283)+mT(:,1);
 elseif Tr<303
       m=((mT(:,3)-mT(:,2))./10).*(Tr-293)+mT(:,2);
   elseif Tr<313
         m=((mT(:,4)-mT(:,3))./10).*(Tr-303)+mT(:,3);
     elseif Tr<323
          m=((mT(:,5)-mT(:,4))./10).*(Tr-313)+mT(:,4);
      elseif Tr<333
             m=((mT(:,6)-mT(:,5))./10).*(Tr-323)+mT(:,5);
         else
             disp('no data for the henry constant exists at this temperature');
             return
         end



ma=[m(1);(2000000)];                               %   [-]         Vector containing
henry constants


%   MOLECULAR MASSES
MO2=32e-3;                                         %   [kg/mol]     Molecular mass of
oxygen
MN2=28e-3;                                         %   [kg/mol]     Molecular mass of
nitrogen

Mna=[MO2;MN2];                                     %   [g/mol]     Vector containing
molar masses of N2 and O2


%   DIFFUSION THROUGH LIQUID (WATER)
%   for a thorough explanation of the derivation of the diffusion coefficient see the
file Syg_Dat.m at liquid diffusities.

VaN2=0.0312;                                            % [m3/kmol] diffusion volume of
N2 (coulson and richardson deel 1 blz 585)
DifLO2= 7.500000000E-11*(Tr-273) + 9.083333333E-10;     % [m2/s] linear relato\ion
derived from experimental data for the diffusion
                                                        % of O2 in water. R2 =
9.971047034E-01
DifLN2=(1.173e-16*2.26^0.5*18^0.5*Tr)/(vis*VaN2^0.6);   % [m2/s] relation for diffusion
coefficient N2. 2.26 is the association factor of the
                                                        % solvent in this case water
and 18 is the molecular weight of the solvent.


DifLa=[DifLO2;DifLN2];
```

```
Oxg_dat=[ma Mna DifLa];
```

```
%   Appendix 2-7-7: Mass balances over the membranes

% File derimc.m

function dermbr = derimc(z,VARM,Bavianenballen,Diam,n,k,msg,R,Tr,Psg,Mnsg,Clg);

% ODE describing a bubble colomn
% Mass transfer from gas to liquid
% The variable 'derivs' stands for: dCgo/dx,dFvg/dx,dPx/dx
% Used by: homoproef.m

%   VAR=[Fvg;Px;Cgo;Cgn]
%   Fvg=gas flow profile over column (air)
%   Px= Pressure profile over column
%   Cgo=Concentration of oxygen in the bubbles
%   Cgn=Concentration of nitrogen in the bubbles



Csg=VARM(1:4);
Fvsg=VARM(5);
Clg1=[Clg;Csg(4)/msg(4)];
dFsgdx=(-pi.*Diam*R*Tr*n.*sum(k.*(Csg./(Mnsg.*msg)-Clg1./Mnsg)))./Psg;      %
[mol/s/m]    Diff. equ. Conc (derivs from mole.balan)
dCgodz=(-pi*Diam*n.*k.*((Csg./msg)-Clg1)-Csg.*dFsgdx)./Fvsg;
dermbr = [dCgodz;dFsgdx];                                                   %   [-]
vector containing the differential equations
```

```
%   Appendix 2-7-8: Mass balances over the gas bubbles

% File deriv.m

function derivs = deriv
(x,VARI,Bavianenballen,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem);

% ODE describing a buble colomn
% Mass transfer from gas to liquid
% The variable 'derivs' stands for: dCgo/dx,dFvg/dx,dPx/dx
% Used by: homoproef.m

%   VAR=[Fvg;Px;Cgo;Cgn]
%   Fvg=gas flow profile over column (air)
%   Px= Pressure profile over column
%   Cgo=Concentration of oxygen in the bubbles
%   Cgn=Concentration of nitrogen in the bubbles



Cg=VARI(3:length(VARI));
phi=VARI(1);
P=VARI(2);
rhog=sum(Cg);
vgs=phi/Acfree;
vg=0.2;                                                             %   [m/s]
superficial gas velocity
hld=vgs/vg;
a=6*hld/(db);
kl=(2+0.66*((rho*0.25*db)/(vis))^(0.5)*(vis./(rho*DifLa)).^(1/3)).*(DifLa./db);
kla=kl.*a;

dPxdx=-(1-hldgem).*rho*g;                                           %   [Pa/m]
Diff. equ. press
dFvgdx=(-R*Tr*Acfree.*sum((kla.*Cg)./(Mna.*ma))-phi.*dPxdx)./P ;    %   [m3/s/m]
Diff. equ. flow (derivs from overall mol.balan)
dCgodx=(-Acfree.*kla.*(Cg./ma)-(Cg.*dFvgdx))./phi ;                 %   [kg/s/m]
Diff. equ. Conc (derivs from mass.balan)
derivs = [dFvgdx ; dPxdx; dCgodx];                                  %   [-]   vector
containing the differential equations
```

```
%   Appendix 2-7-9: Mass balances over the gas bubbles

% File deriv.m

function derivs = deriv
(x,VARI2,Bavianenballen,Acfree,ma,Mna,rho,g,R,Tr,db,Aper,vis,DifLa,hldgem0z,L0);

% ODE describing a buble colomn
% Mass transfer from gas to liquid
% The variable 'derivs' stands for: dCgo/dx,dFvg/dx,dPx/dx
% Used by: homoproef.m

%   VAR=[Fvg;Px;Cgo;Cgn]
%   Fvg=gas flow profile over column (air)
%   Px= Pressure profile over column
%   Cgo=Concentration of oxygen in the bubbles
%   Cgn=Concentration of nitrogen in the bubbles



Cg=VARI2(3:length(VARI2));
phi=VARI2(1);
P=VARI2(2);
rhog=sum(Cg);
vgs=phi/Acfree;
vg=0.2; %   [m/s]   superficial gas velocity
hld=vgs/vg;

%find average hold-up above current x
xover=find(L0>=x);
hldgem=sum(hldgem0z(length(hldgem0z)-length(xover)+1:length(hldgem0z),1))/length
(xover);

a=6*hld/(db);
kl=(2+0.66*((rho*0.25*db)/(vis))^(0.5)*(vis./(rho*DifLa)).^(1/3)).*(DifLa./db);
kla=kl.*a;
%if hld <= 1;
dPxdx=-(1-hldgem).*rho*g;                                            %   [Pa/m]
Diff. equ. press
dFvgdx=(-R*Tr*Acfree.*sum((kla.*Cg)./(Mna.*ma))-phi.*dPxdx)./P;      %   [m3/s/m]
Diff. equ. flow (derivs from overall mol.balan)
dCgodx=(-Acfree.*kla.*(Cg./ma)-(Cg.*dFvgdx))./phi ;                  %   [kg/s/m]
Diff. equ. Conc (derivs from mass.balan)
derivs = [dFvgdx ; dPxdx; dCgodx];                                   %   [-]   vector
containing the differential equations
```

Appendix 3:
Gasification

Appendix 3-1: Gasification and pyrolysis

Pyrolysis kinetics

The pyrolysis reaction was given to be:

$$C_{42}H_{60}O_{28} \rightarrow aCO + bCO_2 + cH_2O + dH_2 + eC_{16}H_{10}O_2 + fC_{28}H_{34}O_9$$

Schröder [2004] determined a proximate product composition of 30 mass percent char, 30 mass percent tar and the balance being gases.

The overall reaction can be broken down into elemental balances. This yields the following system of equations:

$$C - balance : a + b + 16e + 28f = 42$$

$$H - balance : 2c + 2d + 10e + 34f = 60$$

$$O - balance : a + 2b + c + 2e + 9f = 28$$

This system still has 1 degree of freedom left. Therefore the following assumption is made based on results generated by Aspen. The most obvious and clear assumption is that the coefficients of CO and H_2 are equal. If no specific measures are taken to improve the H_2/CO ratio, this ratio will be around 1.

With this assumption the system can be solved.

$$a = 1.39$$

$$b = 3.3$$

$$c = 12.08$$

$$d = 1.39$$

$$e = 1.30$$

$$f = 0.59$$

The reaction scheme for pyrolysis showed 5 reactions. The reactions were depicted as follows:

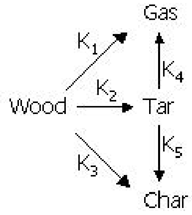


Figure 1. Reaction scheme for wood pyrolysis. Adapted from Mousques [2001]

Assumptions for calculation

The following assumptions are made in order to be able to model the gasification process kinetics followed by the reasoning and a justification:

1. The process is operated in steady-state

Reasoning: If a process is operated in steady-state, there are no temporal differences in the reactor.

Justification: The process is continuous; common assumption

2. Instantaneous particle drying and devolatilisation

Reasoning: The absence of moisture eliminates the need for a moisture diffusion model.

Justification: The temperature difference between feed and reactor is large enough to ensure complete devolatilisation.

3. Plug-flow bed/free-board

Reasoning: This is a simple reactor model. There are no internals; so a packed bed is not an option.
Justification: Real-time gas behaviour resembles plug-flow.

4. Ideal mixing of the solid char

Reasoning: If the char is ideally mixed, there are no char concentration profiles
Justification: Radially distributed feed, with no horizontal profiles, because of assumption of plug-flow behaviour.

5. No ash conversion

Reasoning: Ash conversion yields very unwanted by-products (e.g. toxic metal oxides), and conversion is very low.
Justification: Low ash conversion in a real gasifier.

6. Isothermal behaviour

Reasoning: No thermal gradients over the reactor. This simplifies the kinetic mass and energy balances.
Justification: Insulation can guarantee near-isothermal conditions.

7. Ideal gas behaviour

Reasoning: This is one of the first assumptions when using with gases under medium pressure.
Justification: Small molecules, high temperatures, and medium pressure, so theory is valid within certain allowed error margins.

8. Spherical uniform particles

Reasoning: Particle size distributions can be omitted.
Justification: Previously stated assumption [De Jong 2003]; not large impact on model accuracy.

9. No abrasion, agglomeration, fragmentation, entrainment of solids

Reasoning: These are very complex processes that do not add much value to the general understanding of the process.
Justification: Solids are not the desired products and are therefore of reduced importance.

RRStiff model

In order to model gasification, two different files were needed. The first file contains the fast pyrolysis of the wood feed. The second file contains the tar reactions (reactions 4 and 5) and the gasification. These reactions are modelled in a different file, because the pyrolysis takes only a few milliseconds to take place, whereas the rest of the reactions take much longer. When plotting these results together, information might be lost.

The following parameters were chosen in order to perform the necessary calculations:

T_{in},	25	Temperature at the entrance [*ºC*]
T	1000	Temperature at the exit [*ºC*]
C_w	741.1	Concentration of wood [mol/m^3]
r_{wood}	750	Density of wood [kg/m^3]
f_m	1550	Mass flow of wood [kg/s]
X	1	Conversion of wood in pyrolysis [-]
H	3	Height of the reactor [m]
D	1.2	Diameter of the reactor [m]
v_f	1	Fluidisation velocity [m/s]

These assumptions were approved by ir. De Jong [appendix 8-1], who is an expert on biomass gasification.

The volume of the imaginary pyrolysis reactor, V, and the volumetric flow rate of wood, ϕ_v were calculated by the following equations:

$$V = \frac{1}{6}\pi D^3$$

$$A = \frac{1}{4}\pi D^2$$

$$\phi_v = \frac{\phi_m}{\rho_{wood}}$$

For pyrolysis kinetics the following general equation is used,

$$\frac{dX_i}{dx} = k_i\,(1 - X_i)\left(\frac{V}{\phi_v}\right)$$

where i is gases, tar or char.

The concentrations of the gases are determined as fractions of the total gas concentration according to the overall pyrolysis stoichiometry as described above.

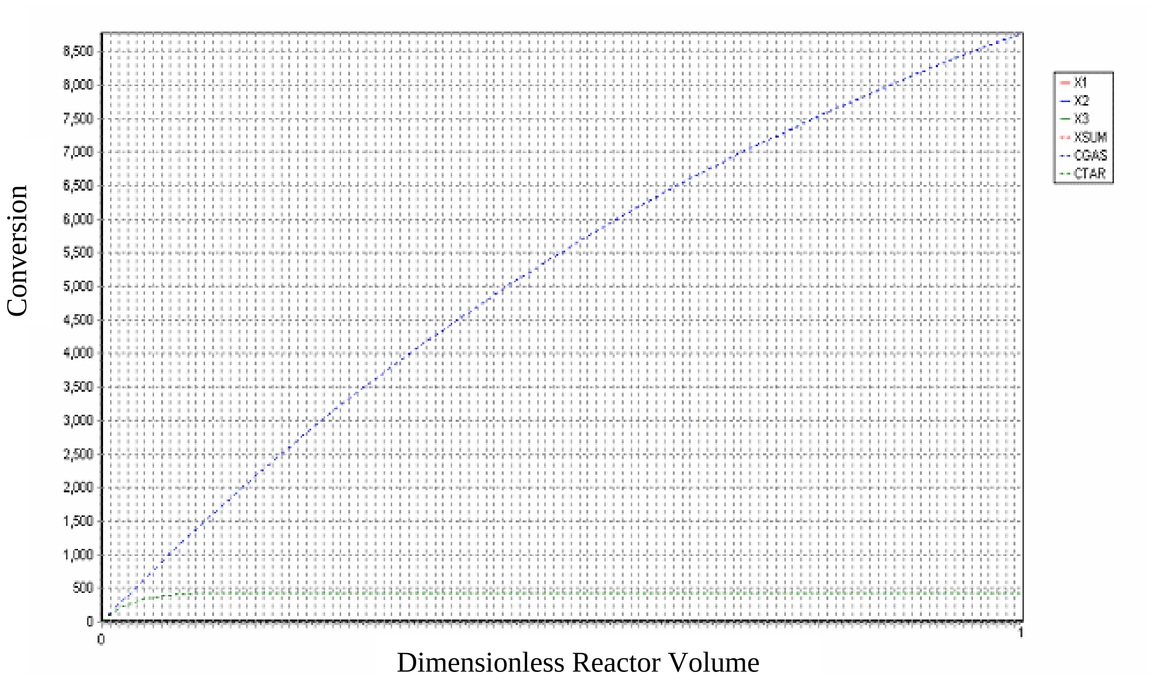


Figure 2. Concentration profiles of tar and gases in the pyrolysis

In gasification the volumetric flow rate is measured by the flow rate of the gases. This parameter has a different value than the volumetric flow rate of wood. The volumetric flow rate of the gases is determined by the following equation:

$$\phi_v = A v_f$$

Because the flow rates differ, the concentrations of the gases in the pyrolysis and the gasification are also different. In order to determine the concentrations in the gasification, the number of moles of gas produced in the pyrolysis is determined by multiplication of the pyrolysis concentrations by the volumetric flow rate of wood. Division of the numbers of moles by the new volumetric flow rate then yields the concentrations of the gases in the gasification section.

The kinetic equations for the various gasification reactions were given in chapter 4. The concentration profiles of the components are determined by the following equation,

$$\frac{dC_i}{dx} = \sum n_{ij} r_j \left(\frac{V}{f_v} \right)$$

where ν_{ij} is the stoichiometric coefficient for component *i* of reaction *j*.
RRStiff reported the following concentration profiles for the gasification.

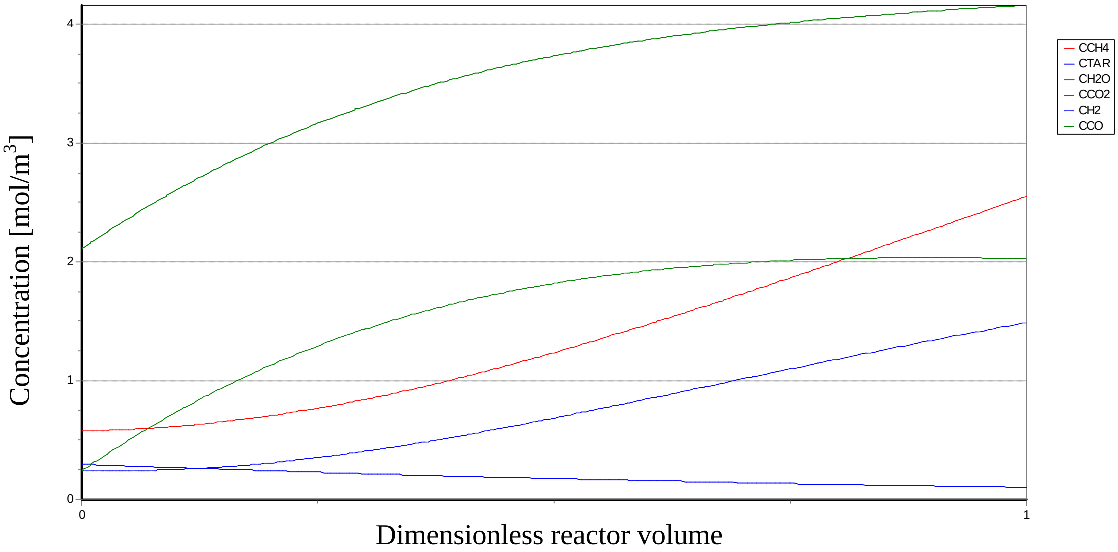


Figure 3. Concentration profiles in gasification

Heat balance

For the heat balance pyrolysis can be described as a single reaction. The overall reaction suffices for the heat generation by the reactions.

$$\frac{dH}{dt} = -\Delta_r H_{1000^\circ C} r_p f_v$$

In this equation the $\Delta_r H_{1000^\circ C}$ is the reaction enthalpy at 1000 °C, r_p is the overall reaction rate of pyrolysis. There are no convection terms in this equation, because the system is operated under isothermal conditions. There is therefore no difference in heat content of the different streams. The reaction enthalpy at 1000 °C can be calculated by the following equation:

$$\Delta_r H_{1000^\circ C} = \Delta_r H_{25^\circ C} + \sum_i u_i C_{P,i} \left(T - T_{ref} \right)$$

The heat balance of the gasification reactions can be derived in a similar manner.

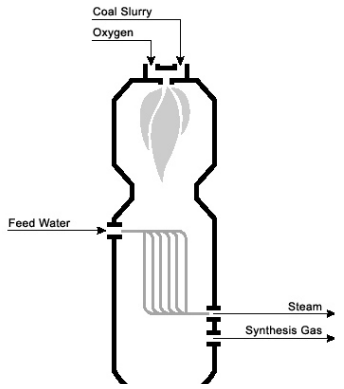
$$\frac{dH}{dt} = f_v \sum_i \left(-\Delta_r H_{1000^\circ C,i} \right) r_i$$

Appendix 3-2: Gasification Reactor types

Coal gasification and biomass gasification are very similar to each other. Therefore it is worthwhile to consider the reactors used for coal gasification. In this appendix the various types of reactors used in coal gasification will be explained first.

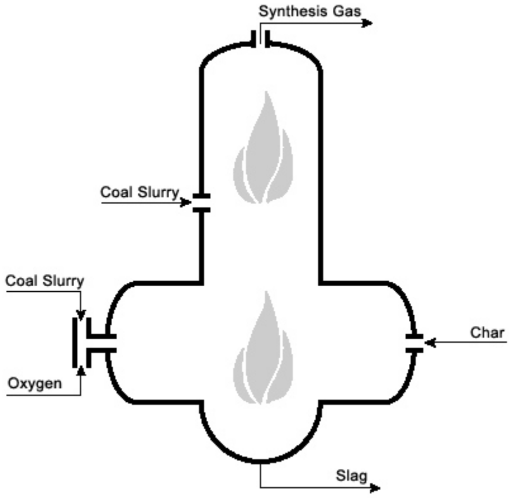
Texaco entrained flow

In the Texaco entrained flow reactor the coal is entered from the top, together with air. The produced syn-gas is cooled in the vessel by heating water to produce high-pressure steam.
The produced syn-gas leaves the reactor at the side of the reactor. Below the syn-gas exit there is a water pool, in which the slag that is left, is dissolved. This black water leaves the reactor over the bottom, and is recycled.



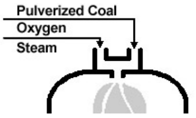
E-GAS Entrained flow

The E-GAS coal gasifier uses slurry feed. The feed flows upward through the reactor in two separate stages. In the first, lower, section about 80% of the feed is gasified with oxygen. The reaction also produces coal ash, but because of the high temperatures (1300-1400 ºC), the produced ash is then converted to molten slag. The slag leaves the reactor in the bottom. In the second section the hot gases are used to devolatise the remaining 20% of the feed. This endothermic reaction reduces the temperature to about 1000 ºC. char is also formed in this reaction, but because only 20% of the feed is reacted at this temperature, the yield is quite low.



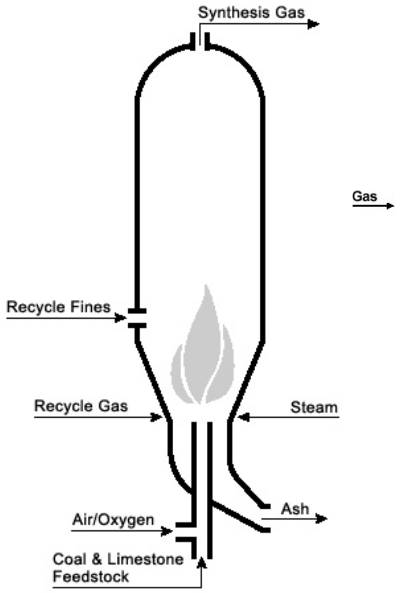
Shell entrained flow

The Shell gasification process consists of the following three stages. The first stage is air-steam gasification at a temperature of about 1350 ºC. Then the effluent is cooled, while generating high-pressure steam. In the lowest unit the produced ashes are removed by scrubbing with water. The high temperature reduces the yield of higher hydrocarbons.
Any ashes that are produced in the process are processed in the same manner as in the Texaco entrained flow reactor, e.g. with a water bath. Some of the slag is deposited on the walls of the gasifier, but that is not a problem.



KRW fluidised bed

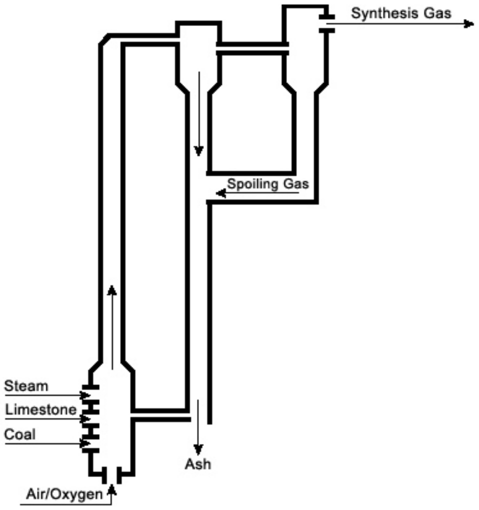
In the KRW gasifier the coal feed enters the bottom, whereas steam and air are added at a higher point in the reactor. The feed mixture is led through concentric high velocity jets to assure good mixing of all reactants. In the gasifier the volatile components burn, which supplies the necessary heat for the



endothermic steam gasification. Solids that have not reacted are pushed to the side of the reactor by the combusted volatiles, and therefore recycled to the central jet. This recycle also improves heat transfer over the reactor. The char is reacted with steam, to produce fuel gas.
The reactor configuration is such that also small particles of coal can be converted. For the coal gasification also lime is added to remove the sulphur and convert it to CaS. This leaves the reactor with the ashes, which are oxidized to $CaSO_4$, which is inert.

Kellogg transport reactor

A characteristic of the Kellogg transport gasifier is that the feedstock consists of very small particles. It is still in the development phase. Fresh feed, air and steam are mixed in the mixing zone, where the gasification reactions also take place. The air is entered from the bottom to facilitate mixing. The product gases **evaporate** from the mixing zone. The gases are then led through a cyclone, where entrained solids are separated from the gas, and led back to the mixing zone. The resulting gas is led through a second cyclone to ensure that there are no particles left in the product gas.

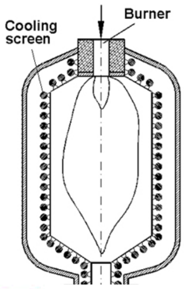


Lurgi Dry Ash

The Lurgi dry ash reactor is a moving-bed reactor that operates in a counter-current manner. The coal enters from the top, whereas the oxygen and steam enter from the bottom. This mode of operation leads to a temperature gradient over the bed, because combustion takes place in the lower part of the reactor (approximately 1000 ºC), whereas the gasification occurs in the top part of the reactor (approximately 250 to 550 ºC).

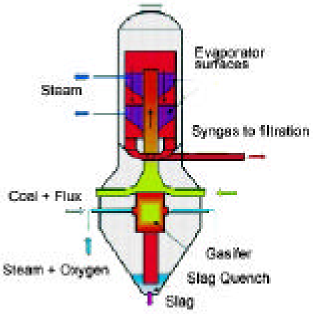
Future Energy entrained flow

The Future Energy entrained flow reactor is a single-stage gasifier. The reactants are fed at the top of the gasifier. The product and the slag are quenched with water. A cooling screen surrounds the gasification chamber. The type of screen depends on the ash content of the feedstock.



Prenflo entrained bed

The Prenflo gasifier combines the gasification and the cooling of the resulting syn-gas into one unit. In the lower part of the reactor the air-steam gasification takes place. The produced syn-gas is then led through a heat exchange section where the syn-gas is cooled from 800 ºC to about 380 ºC, while producing steam. The slag that is formed during the gasification is quenched in a water bath that is below the feed section.



Biomass reactors

A summary of gasification reactors used for biomass conversion is given by ECN [2004] and Foley [1983]. Conceptually many of the reactors show great similarity to those used for coal gasification.

However one of the differences in the evolution of biomass gasification technology is that it was often developed for implementation on a very small scale, typically to power vehicles. For instance in Sweden in the middle of the twentieth century around 70,000 vehicles operated on mobile wood gasifiers. By comparison many of the processes devised for coal gasification were developed during the oil crisis of the 1970’s with the intention of industrial scale production of fuels using Fischer-Tropsch synthesis.

Due to the difficulty of processing raw biomass to produce a suitable feedstock and tar formation, processes have been developed which attempt to address both these problems. One process which has been implemented and which can produce synthesis gas of suitable composition in appropriate quantities from biomass is the Carbo-V® process [Rudloff 2003].

This process recently moved from the pilot phase into the first industrial scale implementation. The process is used to produce a gas suitable for production of methanol or for use in Fischer-Tropsch synthesis. For this reason it is considered to be very suitable for the application considered in this design.

The process, which is shown in Figure 0-1, can be described as follows.

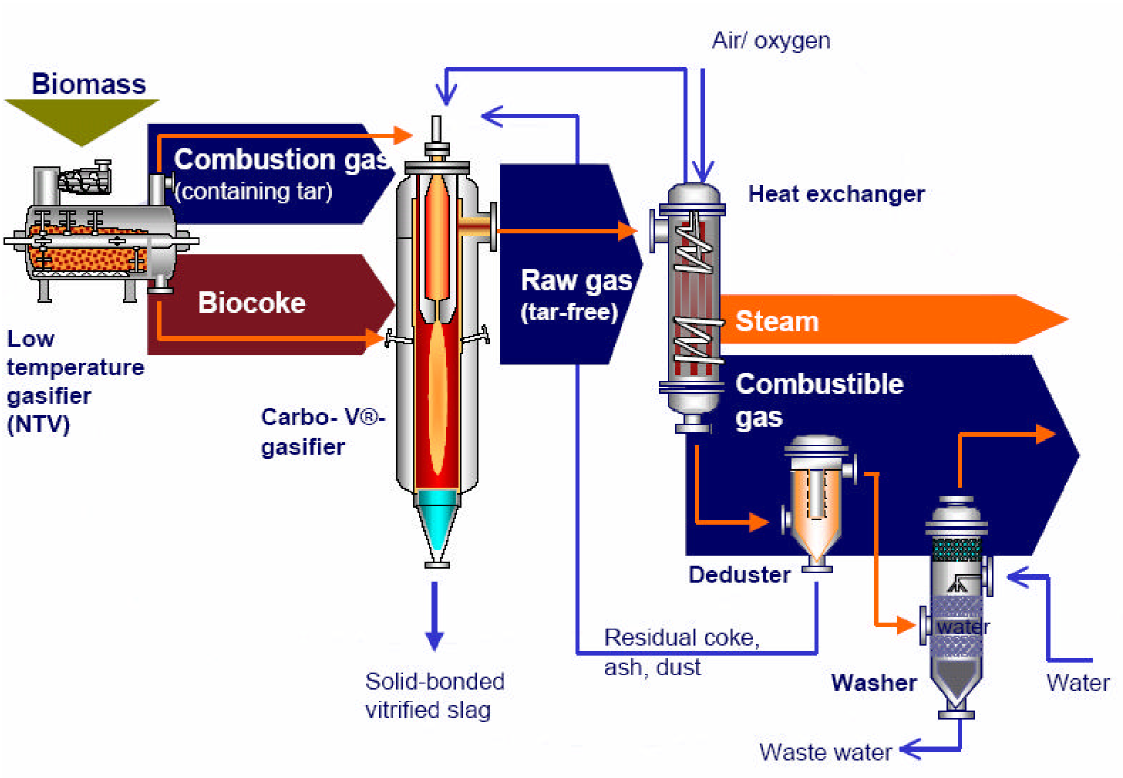


Figure 0-1: Carbo-V® process

The biomass enters the low temperature gasifier. The dominant process in this unit is pyrolysis. The unit produces a tar rich gas and a coke stream.

The tar rich gas is led to the combustion chamber where it is mixed with air/oxygen and residues removed downstream. The mixture is combusted and reaches temperatures up to 1500 K. The temperature used will be partly determined by the slagging temperature of the ash, the limits of the construction material and whether oxygen or air is used. These conditions result in complete conversion of the tars in to CO, H_2, CO_2 and other small molecules, the ash is melted to form liquid slag.

The hot gases and liquid slag leave the combustion chamber and enter the high temperature (1100 K) gasification section. In this section finely ground coke is added. The hot gases react with the coke by means of endothermic reactions. This converts the thermal energy developed in the combustion section into chemical energy. The slag solidifies and collects at the bottom of the section. The gases pass along the outside of the combustion chamber where they react further and absorb more heat, they then leave the gasification section.

In the following section the hot synthesis gas is cooled by counter-current heat exchange with the air entering the system. Any residual heat is used to produce steam.

The residual solids (such as ash or coke) are removed from the synthesis gas by a cyclone. The solids are returned to the combustion chamber where they are either gasified or converted to slag. In the final step, which may or may not be necessary prior to the fermentation, the synthesis gas is passed through a washer to remove any residual particles and also gases such as H_2S.

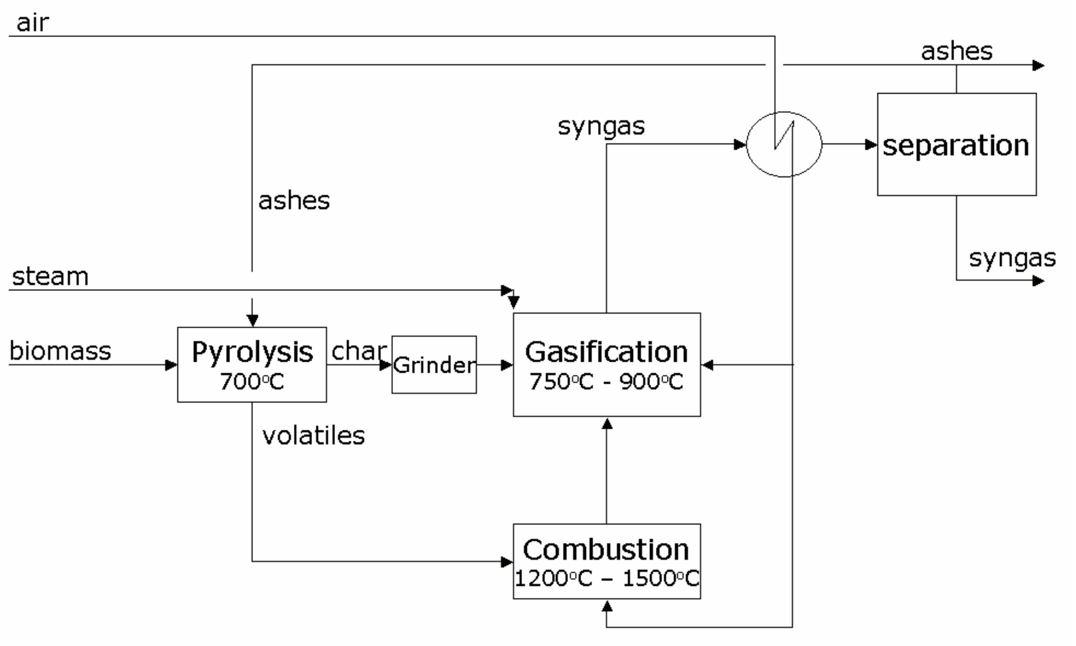
Appendix 3-2: Gasification reactor types

This process has been shown to convert biomass to synthesis gas with a cold-gas efficiency of 81.9%. What is interesting is that up to now the process has been used to produce methanol and diesel, both of which are relatively low value products and in the case of diesel extremely strict rules apply regarding the maximum sulphur content.

Further it can be mentioned that the Carbo-V process resembles the biomass gasification process as described in the patent of Rüdiger [1997].

According to the patent DE 196 18 213 A1 [Rüdiger H., 1997] the pyrolysis, gasification and combustion steps can be combined in a very efficient way. First biomass is pyrolysed, and 2 separate streams are produced. The gas/vapour part produced in this step is led to a combusting chamber, in which syn-gas is formed at 1200-1500ºC. In this combustion chamber small molecules such as CH_4, H_2, CO_2 and CO are thermodynamically preferable and the tar and other undesired components are converted. This syn-gas is fed into the in a gasification chamber where the solid part is gasified at 800-850ºC. The exothermic reactions taking place in the gas/vapour converter are used to drive the endothermic reactions in the char gasification section.

They give the following flow scheme:



The Biosyn process

The process is based on a bubbling fluidised bed operating up to 1.6 MPa. A 10 tonnes per hour plant has been built. Thermal efficiency varies from 70-80%. The product gas contains mostly syn-gas and CO_2, a little tar and dust has to be removed. HHV values vary form 6-12 MJ/Nm^3 depending on the gasifying agent.

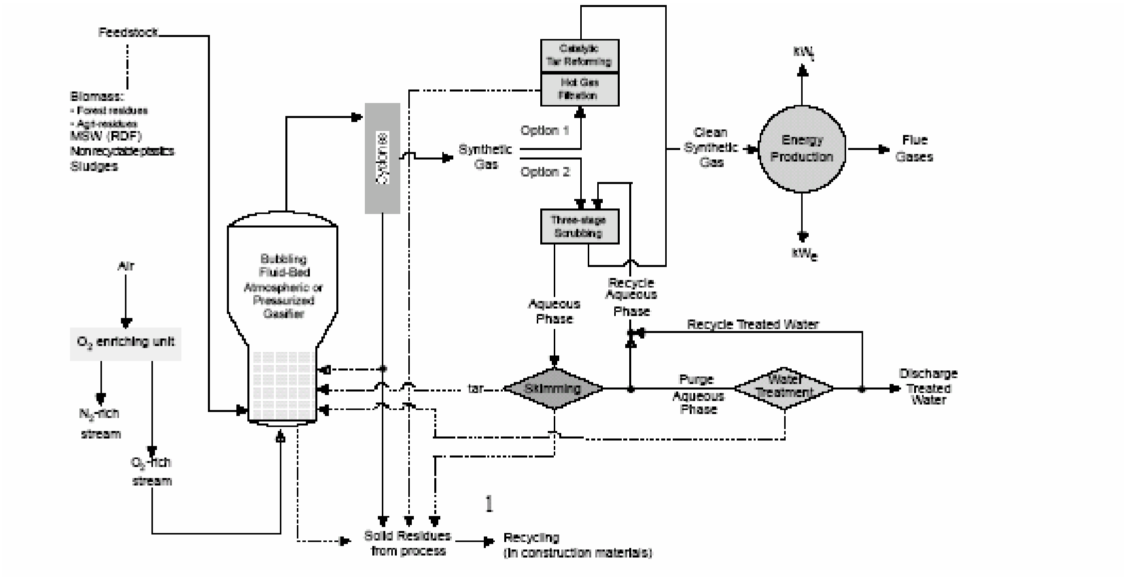


Figure 2. The Biosyn proces

The SilvaGas Process

This low-pressure process consists of two distinct reactors; a gasification reactor and a combustion reactor. Char from the gasifier (850-1000ºC) is led to the combustor where the heat needed for the gasifier is generated. Heat transfer is accomplished by circulating sand between the two reactors. A 200 tonnes per day plant has been built, feeding steam:biomass at a ratio of 0.45:1. Product composition is 21% H_2, 43% CO. The rest is mainly CO_2 and methane. No nitrogen is present in the product gas because the combustion is separated from the gasification.

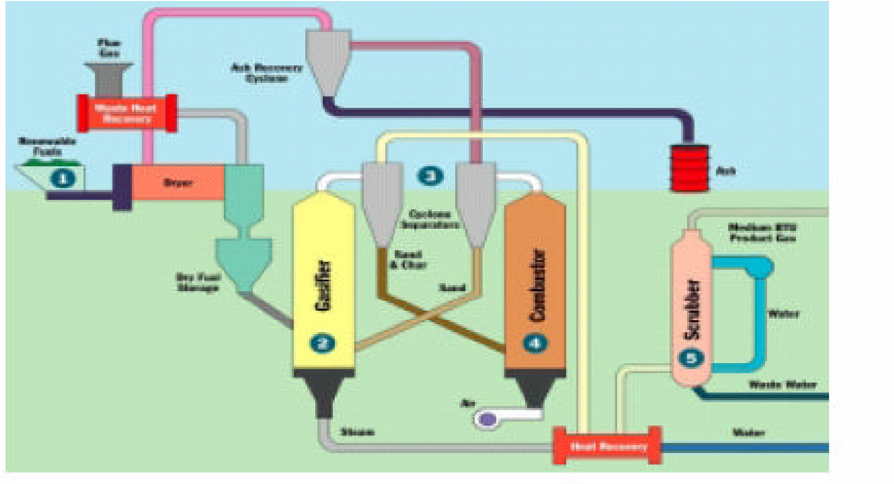


Figure 3. The Silvagas process

The Renugas process

This is a 20 bar pressurised bubbling fluidised bed, 12 and 100 tonnes per day (2 versions exist), 850ºC. Syn-gas composition is 19% H_2, 26% CO, 37% CO_2 and 17% methane.

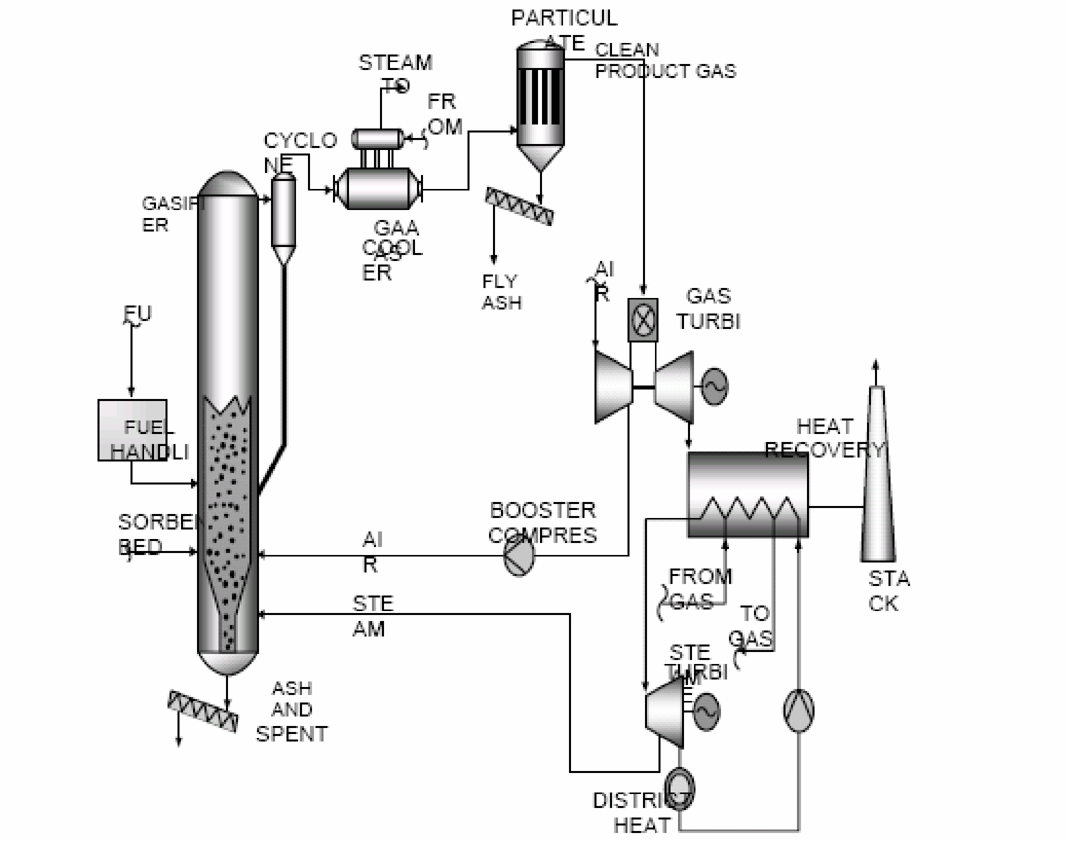


Figure 4. The RENUGAS process

The Fast Internal Circulation Fluidised Bed (FICFB) process

This process looks like the Silva process. Slight differences determine its output:

Hydrogen	30-45 vol.%
Carbon monoxide	20-30 vol.%
Carbon dioxide	15-25 vol.%
Methane	8-12 vol.%
Ammonia	500-1000 ppm
Nitrogen	1-5 vol.%
Hydrogen sulfide	20-50 ppm
Tar	0,5-1,5 g/Nm³
Particles	10-20 g/Nm³

Type of plant	Demonstration plant	
Fuel Power	8000	kW
Electrical output	2000	kW
Thermal output	4500	kW
Electrical efficiency	25,0	%
Thermal efficiency	56,3	%
Total efficiency	81,3	%

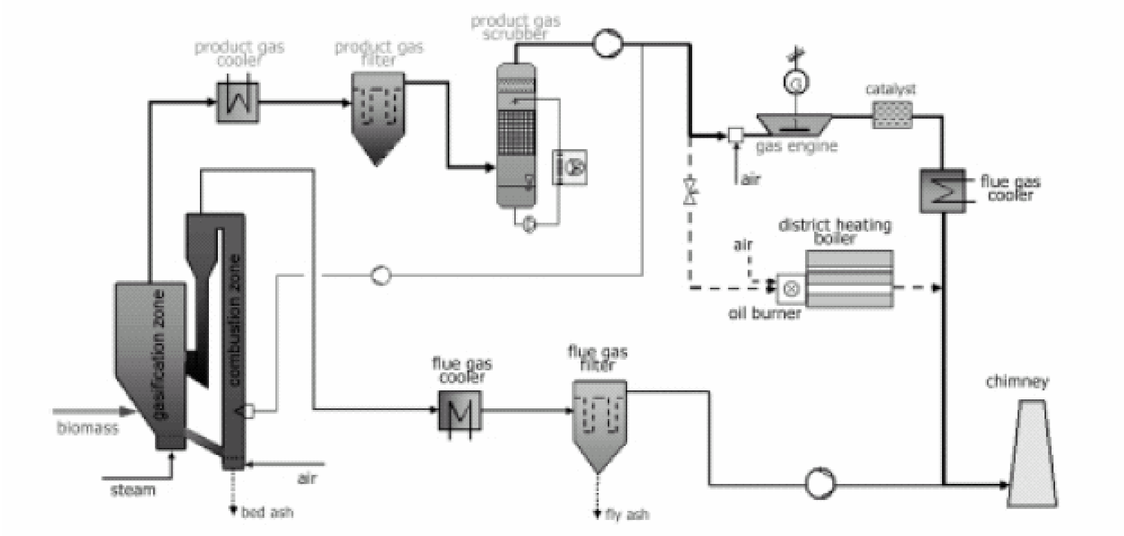


Figure 5. FICFB Gasification process

A last note to this document: Many different designs were found, even more than depicted here. Some resemble each other but will certainly be operated differently.

Appendix 3-3: Gasification design

Crusher

Selecting a proper crusher was not very easy. Aspen and Coulson & Richardson [2000] gave different recommendations and searching the world wide web didn't help much too. Aspen advised a jaw crusher, but this will never yield the right particle sizes. Furthermore, the power as indicated by Aspen is far too low. For wood a Bond Work Index is 45.

According to Coulson & Richardson [2000] wood is solids class 4. A hammermill, disk mill or ball mill is recommended.

Contacting several machine builders was decisive. Typical dimensions and data were obtained as well as pictures. Prices ranged from second hand crushers costing €7,500 to brand new ones of €125,000. Typical dimensions were taken from the various crushers, adapted to the needs of this project. An average price (€60,000) was chosen, as it can be argued that €125,000 is quite high. These data are given in the Crusher Specification Sheet.
This price estimation is supported by Coulson & Ricardson [2000].

<u>Below the information form the machine builders is given:</u>

Rictec Pte Ltd, Singapore

```
Dear sirs,

We have one unit MP-75 for sales (2nd hand). Only in used for less than
2 weeks. Still in PRIME CONDITION. BRAND NEW at USD$ 125,000.00. Now,
owner want to sell off at USD$ 60,000.00 less than half price Ex-works
Singapore.

First come first serve. Immediate response to secure. Shredding
capacity
+- 6 tons per hour.

Owner in Singapore dealing with wood wastes recycling. They have
acquired a high capacity wood wastes shredder (one hour 45 tons
shredding capacity).

Therefore, they want to sell off the smaller unit.

Please see attachments.

Best Regards,

Philip Ong (Managing Director)
Rictec Pte Ltd
794 Upper Bukit Timah Road #02-08 Singapore 678136
Tel: +65 6763-3618
Fax: +65 6769-6033, +65 6565-0380
Mobile: +65 9663-1819
Email: rictec@rictec.com.sg
Email: rictec@singnet.com.sg
Web: http://rictec.com.sg
```

Figure XXX The MP-75 from Rictec

MLS Machinery Inc.

51 Esna Park Dr., Unit 4
Markham, Ontario
Canada
L3R 1C9

Tel: (905)731-6369
Fax: (905)731-4639
Email: beatriz@mlsmachinery.com

We are pleased to submit the following for your consideration and approval.

JACOBSON [XLT-24326] - VERTICAL FEED HAMMER HOG

Capacity 150 HP 3560 rpm motor, inlet size 26-1/2" x 10-1/2", top loading, screen 1/4" diameter, feed estimated at 2-3 tons/hr. Voltage: 460/3/60.

COND: Good

Yr of manuf: 92

PRICE: (US) _______________ $7,500

Appendix 3-3: Gasification design

Figure XXX The Jacobson [XLT-24326] - Vertical Feed Hammer Hog

Trans World Equipment Sales

Dear Sirs,

In response to your email, I am forwarding a couple of pieces of equipment, suggested by our owner, Mr. Riley. He thinks that pieces would be suitable for what you are doing.

http://www.twequip.com/Equipment/g120104.htm
http://www.twequip.com/Equipment/g120104pics.htm
http://www.twequip.com/Equipment/haybusterspecs.htm

http://www.twequip.com/Equipment/k150500.htm
http://www.twequip.com/Equipment/k150500pics.htm

If you could forward all of your contact information, such as: mailing address, telephone, fax, I could send more information on these units. We have manufacturers videos, and some videos of the actual machines, we have, working. And maybe this would aid in your decision on a piece of equipment that will fit your companies needs.

If you need anything else, please don't hesitate to contact me.
Thank You,
Karen Edwards
Trans World Equipment Sales, Inc.
800-542-2940
Ext. 620

The gasification reactor

The dimensions of the fluidised bed are calculated with the help of Excel. For the calculation of the dimensions an assumption has to be made. The assumption is that wood has no influence on the fluidisation behaviour. Also the particles in the bed are assumed to be spherical. Furthermore a few parameters had to be chosen in order to calculate the dimensions. The fluidisation velocity is chosen to be 1 m/s, which is a good value according to the expert De Jong (see appendix 8-1). In the following table several parameters can be found, which are used for the calculation.

diameter particle	$5.00 \cdot 10^{-04}$	m
density particle	2600	kg/m^3
density gas	0.6	kg/m^3
viscosity gas	$4.22 \cdot 10^{-05}$	Pa s

First is the minimal fluidisation velocity calculated, with the following equation:

$$e_{mf} = 0.586 \cdot \Psi^2 \cdot \frac{m_g^2}{r_g \cdot \left(9.81 \cdot \left(r_p - r_g\right) d_p^3\right)^{0.029}} \cdot \left(\frac{d_p}{r_g}\right)^{0.021}$$

The value found for the minimal fluidisation porosity is 0.40. ? in this formula is the spherical volume equivalent diameter of the particle.
With the help of this value the minimal fluidisation velocity can be calculated, the following formula is used:

$$u_{mf} = \frac{\left(y \cdot d_p\right)^2}{150 * m_g} \cdot \frac{9.81 \cdot \left(r_P - r_g\right) \cdot e_{mf}^3}{1 - e_{mf}}$$

The value found with this formula is 0.11 m/s, this is a realistic value according to the expert De Jong. In the literature similar values can be found. The terminal velocity of a particle is then calculated, with the next equation:

$$u_t = \left(\frac{0.0178 \cdot \left(9.81 \cdot \left(r_p - r_g\right)\right)^2}{\left(r_g \cdot m_g\right)^{1/3}}\right) \cdot d_p$$

The value found for the terminal velocity is 3.85 m/s.
Now the maximum bubble diameter can be calculated with the following formula:

$$d_{pm} = 0.652 \cdot \left(A_c \cdot \left(u_0 - u_{mf}\right)\right)^{0.4}$$

The A_c in this equation represents the column diameter, this is calculated with the amount of gas we use to fluidise divided by the fluidisation velocity which is chosen to be 1 m/s. The maximum bubble diameter is then 1.64 m. By calculating the bubble diameter at a certain height is can be avoid that the diameter will be greater that the actual column diameter. From the area of the column followed the diameter of the column, using the following relation.

$$d_c = \sqrt{\frac{A_c}{1/4 \cdot p}}$$

The following relation is used to calculate the bubble diameter at a certain height in the bed.

$$d_b = d_{bm} - d_{bm} \cdot \exp\left(-0.3 \cdot \frac{h}{D_c}\right)$$

In this relation is *h* the certain bed height and D_c is the column diameter.
The average bubble rise velocity, is calculated with the next equation:

$$u_b = u_0 - u_{mf} + 0.71 \cdot \left(\left(9.81 \cdot d_p\right)^{0.5}\right)$$

The values found here is 1.09 m/s.
The following value, which is calculated is the fractional of bubbles, which occupy the bed.

$$d = \frac{\left(u_0 - u_{mf}\right)}{\left(u_b - u_{mf} \cdot \left(1 + a\right)\right)}$$

The bed height can be chosen now, the residence time of the reactant in the reactor depend on this value. The residence time for fluidised bed gasifiers are a few seconds, there is chosen for a bed height of 3 m. The volatile components then have a residence time of a few seconds, which is a reasonable value.
The following dimensions are:

Diameter column	1.2 m
Height of the bed	3 m
Fluidisation velocity	1 m/s

The height for the freeboard is chosen to be 5 meter, this is sufficient for the solid particles to fall back to the bed. The diameter of the freeboard is chosen to be larger is order to prevent pressure build up in the reactor. In the reactor is the amount of gases increasing. The diameter chosen is 1.5 meter.

All formulae are from Scott and Fogler [1999]

Distributor plate design

In order to facilitate a fluidised bed a distributor plate is needed, to distributor the fluidising agent evenly over the bed. So demands are made for the distributor plate, it should be strong, it should have a minimal pressure drop, it should distribute the fluidising agent homogeneously over the bed.

The thickness and the orifice diameter have to be chosen, and be checked if the chosen value are correct.

The following thickness and orifice diameter are chosen. Diameter orfice is 0.004m and the thickness is 0.006m. In the next table can the parameters be found used for the calculations.

u_0	1	[m/s]	Fluidisation velocity
A_c	1.130973	$[m^2]$	Area column
e_{mf}	0.401467	[-]	Minimal Fluidisation porosity
u_{mf}	0.108775	[m/s]	Minimal fluidisation velocity
t	$6.00.10^{-03}$	[m]	Thickness of the distributor plate
d_{or}	$4.00.10^{-03}$	[m]	Diameter hole in distributor plate
H_{mf}	3.5	[m]	Minimal fluidisation height
c	66.7	[-]	Pressure ratio

First the pressure drop over the bed is calculated, with the following equation:

$$P_b = r_p \cdot \left(1 - e_{mf}\right) \cdot H_{mf} \cdot 9.81$$

The pressure drop over the bed is 53431.6 Pa.

The next calculations are done for the calculation of the pressure drop over the distributor plate. For this the pressure ratio had to be determined. Several theories are available to determine this value. The used theory is used of Hiby (1996), in this theory the ratio of the superficial gas velocity and the superficial minimal fluidisation velocity determines the value for the pressure ratio.

$$\frac{\Delta p_b}{\Delta p_d} = 6.7 \qquad \text{for } u_0/u_{mf} \text{ 1-2}$$

$$\frac{\Delta p_b}{\Delta p_d} = 66.7 \qquad \text{for } u_0/u_{mf} >>2$$

In this case the $u_0/u_{mf}>>2$, so the value for the pressure ratio is chosen to be 66.7.

The pressure drop over the distributor plate is then $P_b/66.7=801.1Pa$.

The following parameter that is calculated is the drag coefficient in one orifice, with the following formula.

$$C_d = 0.82 \cdot \left(t / d_{or}\right)^{0.13}$$

The value found for the drag coefficient is 0.864. Now the superficial gas velocity through a hole can be calculated. The following equation is used.

$$u_{or} = C_d \cdot \sqrt{\frac{2 \cdot P_d}{r_g}}$$

The superficial orifice velocity is 44.7 m/s.
The following parameter to be calculated is the number of orifices on the distributors plate, the next equation is used.

$$N_{or} = \left(\frac{u_0}{u_{or}}\right) \cdot \left(\frac{4}{p \cdot H_{mf}^2}\right)$$

Thus 1780 holes are needed.
The distance between the holes can be calculated, with the following equation.

$$pitch = \frac{1}{\sqrt{N_{or}}}$$

The pitch is 0.023m.
The length of a jet through the orifice can be calculated with this formula.

$$L_j = \left(5.25 \cdot \left(\frac{r_g \cdot u_{or}^2}{\left(1 - e_{mf}\right) \cdot r_p \cdot d_p \cdot 9.81}\right)^{0.4} \cdot \left(\frac{r_g}{r_p}\right)^{0.2} \cdot \left(\frac{d_p}{d_{or}}\right)^{0.2} - 4.5\right) \cdot d_{or}$$

The jet length is 0.0016m.
After these calculation a couple of test have be done to see if the bed is stable, and if bubble coalescence occurs. The following equations are used.

$$Check1 = \frac{16 \cdot r_g \cdot u_0}{\left(p \cdot N_{or} \cdot C_d \cdot \left(d_{or}\right)^2\right)^2}$$

$$Check2 = \frac{1.5}{9.81^{0.2}} \cdot \left(\frac{6 \cdot \left(u_0 - u_{mf}\right)}{p \cdot N_{or}}\right)^{0.4}$$

The value found for the first check is 1602.48, which is above 800, value below 800 indicate an unstable bed. The value found for the second check is 0.059, if this value is below the pitch no bubble coalescence occurs. In this case there is obviously premature bubble coalescence, this is not considered to be a major problem.
All the relations can be found in chapter 7 of Philip [2000].

Appendix cyclone dimensions

The cyclone needed to clean the syn-gas from the gasifier was calculated by Aspen. The cyclone chosen was a high efficiency cyclone (0.9).
Figure 1 shows the cyclone geometry. Table 1 shows the cyclone dimensions.

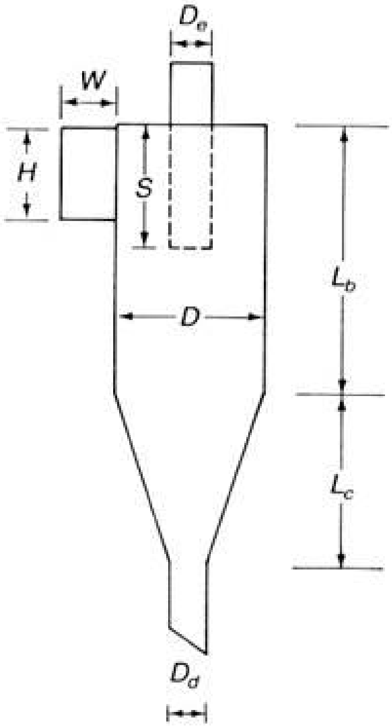


Figure 1. Cyclone Geometry

The Cyclone design configurations are:

Table 1. Cyclone dimensions

Number		1	
Diameter cylinder	D	1.034683	[m]
Efficiency		0.900003	[-]
Length of vortex		2.563529	[m]
Length cylinder	Lb	1.552025	[m]
Lentgh of cone	Lc	2.586708	[m]
Diameter gas outet	de	0.517342	[m]
Length of gas outlet	s	0.517342	[m]
Width of gas inlet	W	0.206937	[m]
Height of gas inlet	H	0.517342	[m]
Diameter solids outlet	Dd	0.388006	[m]
Number of gas turns		7	[-]
Inlet/saltation velocity ratio		1.219685	[-]
Overall height		4.138733	[m]

Appendix 4
Downstream processing

Appendix 4-1: DSP process choices

Numerous alternatives for PHB release and purification have been investigated at the lab scale, only one method has been successfully applied industrially. The various options are described in detail below.

Washing with sodium perchlorite (NaClO)

Washing with NaClO results in chemical decomposition of all cell elements, including the PHB granules, however because of their size and crystallinity the PHB granules are degraded relatively slowly. The technique typically involves addition of the cells to a NaClO solution. An hour later PHB granules are recovered by centrifugation.

Chloroform extraction

In the two extraction processes the PHB granules are dissolved in chloroform, which forms a separate organic phase. The aqueous phase is withdrawn and cell debris is then removed by filtration. Finally high purity PHB is precipitated by addition of an antisolvent. The addition of NaClO dramatically decreases the time required to dissolve the PHB, most likely due to degradation of the PHB chains.

For the pure chloroform process typically 30 times the volume of chloroform is used and the granules require at least 15 hours to dissolve [Ghatnekar 2002]. Addition of NaClO reduces this time to 1.5 hours [Ghatnekar 2002].

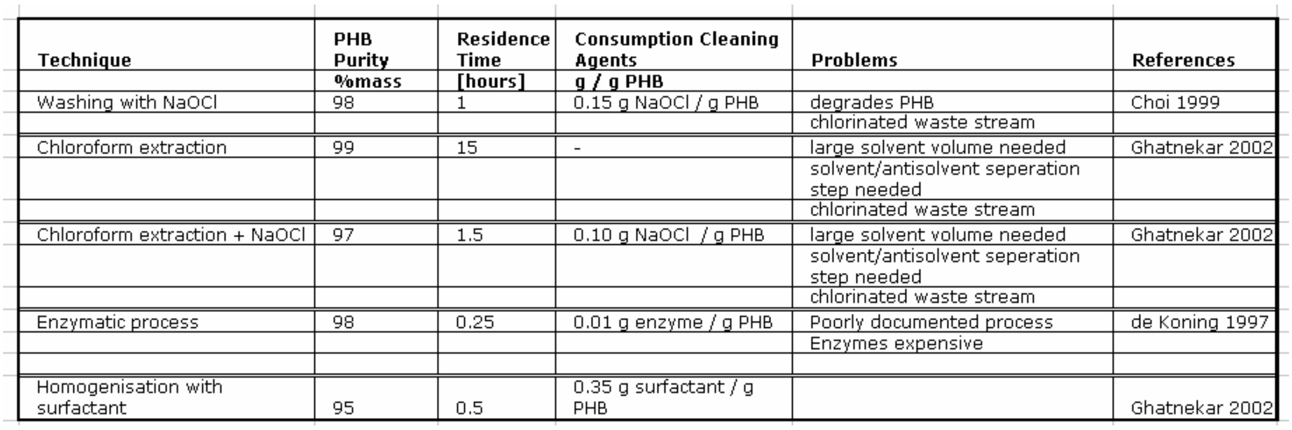
Enzymatic purification

Enzymatic release and purification is the method used by ICI [Babel 2001]. A cocktail of enzymes is added which selectively degrade the other cell components leaving high purity PHB. The main problem is the cost of the enzymes, which is known to be high [Babel 2001]. In addition little, if anything, is known about the cocktail of enzymes required or the processing conditions which are suitable.

Homogenisation with surfactant

Homogenisation of the cells in a SDS (sodium dodecyl sulphate) solution results in the cell debris remaining suspended in the broth and not agglomerating with the PHB granules. The PHB granules can then be separated from the suspension without other cell debris also being collected. However each gram of SDS only solubilises 0.72 grams of debris [Kim 2002]. This would result in a typical rate of SDS consumption of 0.35 kg / kg product.

A summary of all these options is provided in Figure 0-1.



Technique	PHB Purity %mass	Residence Time [hours]	Consumption Cleaning Agents g / g PHB	Problems	References
Washing with NaOCl	98	1	0.15 g NaOCl / g PHB	degrades PHB	Choi 1999
				chlorinated waste stream	
Chloroform extraction	99	15	-	large solvent volume needed	Ghatnekar 2002
				solvent/antisolvent seperation step needed	
				chlorinated waste stream	
Chloroform extraction + NaOCl	97	1.5	0.10 g NaOCl / g PHB	large solvent volume needed	Ghatnekar 2002
				solvent/antisolvent seperation step needed	
				chlorinated waste stream	
Enzymatic process	98	0.25	0.01 g enzyme / g PHB	Poorly documented process	de Koning 1997
				Enzymes expensive	
Homogenisation with surfactant	95	0.5	0.35 g surfactant / g PHB		Ghatnekar 2002

Figure 0-1: Summary of release and purification options

Homogenisation with solvent

At this point it was felt to be worth investigating both the nature of the impurities and to try and find a method more suitable for industrial scale production. The high purity achieved by the use of surfactant (SDS) and enzymes show that PHB granules have a high purity in their natural state and that impurities are concentrated on the granule surface. Impurities are the result of cell debris not separating from PHB during purification, SDS appears to increase the solvation of these impurities which prevents them sedimenting during centrifugation or attaching to the granule surface.

After an extensive study of the literature and discussion with an expert (appendix 8-3) a new method using a solvent consisting of water/tert-butanol (70/30 mass fraction) was chosen for further development. The thinking behind this method is described below.

Dennison and Lovrien [Dennison 1997] describe the purification of protein and other biomolecules using a mixture of water and tert-butanol. These two liquids are perfectly miscible in any ratio, in contrast to n-butanol and water. Purification is achieved because a mixture of the t-butanol and water is capable of effectively solvating both hydrophobic and hydrophilic sections of large bio-molecules. Normally proteins are then selectively precipitated by addition of an ionic antisolvent. The antisolvent causes a second liquid phase, rich in t-butanol, to form by increasing the polar nature of aqueous phase. As the t-butanol content of the aqueous phase decreases protein solubility decreases and it precipitates at the aqueous/organic phase interface.

The requirement of the DSP sub-process is to separate cell debris from PHB. It is highly unlikely that PHB granules would dissolve in the t-butanol/water solvent during the timescale envisaged as it requires 15 hours to dissolve in chloroform, a solvent for which it shows a great affinity. However it is reasonable to expect cell debris to be solvated by t-butanol/water because a surfactant, such as SDS, which also has an amphiphilic character is extremely efficient at solvating cell debris.

This line of reasoning was discussed with an expert on bioseparations (see appendix 8-3) and found to be consistent and logical. It should however be noted that an experiment to confirm the methods efficacy has not been carried out.

Appendix 4-2: DSP unit operations

After the fermentation there is a large train of operations that are needed to recover the product from the broth. This process can be divided into four sub processes. They are the solid/liquid separation, isolation, purification and final upgrading, polishing, of the product. This chapter deals with the different options that are available to the chemical engineer.

Solid/liquid separation

The first step in the down-stream processing is to remove the solids in the broth. The solids are either the micro-organism or the product, depending on whether the micro-organism excretes the product.

Filtration and micro-filtration

The vacuum rotary vacuum filter is the most common filter unit in bio-separations. The pressure inside the drum is semi-vacuum, whereas the pressure outside the drum is atmospheric. Because of the pressure difference the liquid is sucked into the filter, leaving the solids on the outside. The filter slowly rotates, and the filter cake is continuously skimmed off the filter after being washed and dried. Figure 1 shows a filter from the end side.

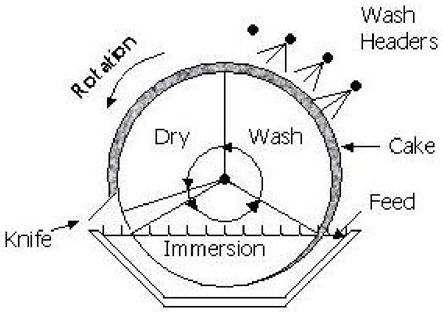


Figure 1. Rotary drum filter. Adapted from Belter (1998)

Heating the feed is a common pretreatment method in order to simplify the filtration. The enzymes of the microorganisms denaturise, which makes them easier to filtrate. [Belter 1998].

Centrifugation

The principle of centrifugation is based on the difference in density between the solvent and the solutes. By spinning around the pressure on the fluid increases, which accelerates the sedimentation process. It has two major disadvantages relative to filtration. It is more expensive and the product contains more solvent than a filter cake. However, when filtration is not possible, centrifugation is very good alternative. [Belter 1988; Krijgsman 1992; Harrison 2003]

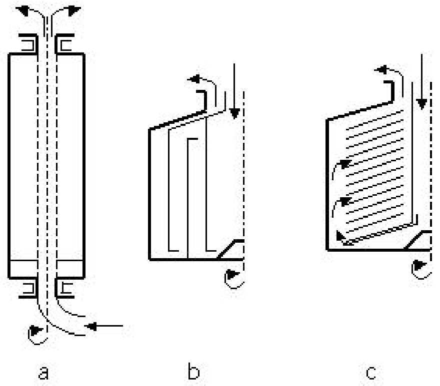


Figure 2. Sedimentation centrifuges. a) tubular centrifuge, b) multichamber, c) disk stack centrifuge. Adapted from Krijgsman [1992]

Cell disruption

When the product is produced in the cell, one of the first steps after the fermentation is to break up the microorganism. There are several techniques available.

Table 1. Cell disintegration techniques. Adapted from Belter [1988]

Chemical methods			
Technique	**Principle**	**Stress on product**	**Cost**
Osmotic shock	Osmotic rupture of membrane	Gentle	Cheap
Solubilisation	Detergents solubilise cell	Gentle	Moderate-expensive
Lipid dissolution	Organic solvent dissolved in cell wall, and so destabilizes it	Moderate	Cheap
Enzyme digestion	Cell wall digested, providing disruption	Gentle	Expensive
Alkali treatment	Saponification of lipids solubilises membrane	Harsh	Cheap

Mechanical methods			
Technique	**Principle**	**Stress on product**	**Cost**
Homogenisation (blade type)	Cells chopped in Waring blender	Moderate	Moderate
Grinding	Cell ruptured by grinding with abrasives	Moderate	Cheap
Ultrasonication	Cells broken with ultrasonic cavitation	Harsh	Expensive
Homogenisation (orifice type)	Cells forced through small hole are broken by shear	Harsh	Moderate
Crushing	Cells crushed between glass or steel balls	Harsh	Cheap

Osmotic shock, detergent solubilisation and lipid dissolution are the most common chemical cell disruption techniques. Osmotic shock is a very simple procedure. The cells are dumped in a body of pure water that is about twice the volume of the cells. The osmotic difference causes the cells to take up too much water, which causes the cell to explode.

Solubilisation occurs by adding a chemical that disrupts the membranes. A volume of chemicals of about half the volume of the cells is needed for this technique. Lipid dissolution works in a similar manner, because a chemical is added to disrupt the membrane by acting on the lipids. The difference lies in the exact mechanism. In solubilisation the lipids are captured in micelles, which causes the cell break, in dissolution the strength of the membrane is worsened because chemicals dissolve, which breaks the structure.

The application of the mechanical methods depends on the scale of the process. Homogenisation in a Waring blender, grinding with abrasives and ultrasonication are most suited for a small-scale application.

Depending on the type of product that is produced in the cell, the length of the homogenisation process should be adjusted. If the homogenisation takes too long, there is a chance that the product is destroyed in the process. [Belter 1988; Krijgsman 1992;Wesslingh 1994; Harrison 2003]

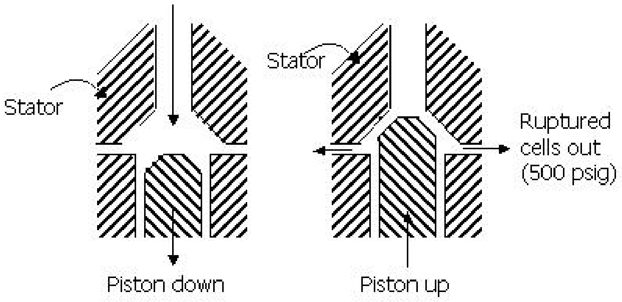


Figure 3. A homogenisation valve. Adapted from Belter [1998]

Isolation

The next step in the down-stream processing is to increase the product concentration in the broth. This can be done by evaporation, extraction, adsorption, and membrane separation. They will be discussed below.

Evaporation

Another way for concentrating the broth is evaporating the water. Many evaporator types have been developed over the years. Figure 4 shows one type of evaporator.

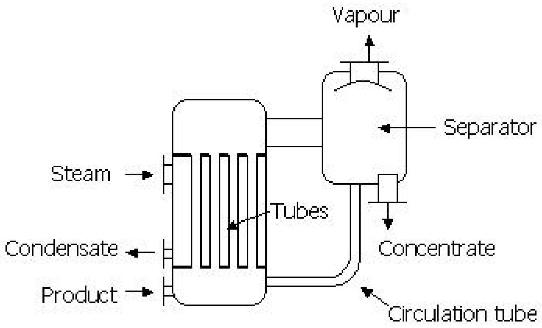


Figure 4. Natural circulation type evaporator. Adapted from Krijgsman [1995]

Evaporation is a very energy intensive procedure, and therefore other possibilities have to be discussed.

Extraction

Extraction is not only used in biotechnology. The basis for the separation can be found thermodynamics. The extractant is a solvent that is immiscible with the feed solvent. The product can be dissolved in both phases, so it will divide over the phases. The extent to which the product diffuses to the other phase determined the amount of extractant needed. Usually more phases are needed to extract most of the product. [Belter 1988; Krijgsman 1992;Wesslingh 1994; Harrison 2003]

Adsorption

The second commonly used process for isolation of the product is adsorption. In adsorption the feed is led over adsorbent particles, where the product is adsorbed by the particles. When the particles are saturated with product, the product is desorbed in another reactor. When the adsorbent is regenerated it can be used again. The adsorbent particles can also be immobilised on a fixed bed. The design of an adsorber is not easy, because the kinetics are not linear in time and space.

Adsorption is usually more selective than extraction. It is mostly used for the separation of proteins. A disadvantage of adsorption is the handling of solids. Also the scale-up of a fixed-bed reactor may prove to be quite difficult. [Belter 1988; Krijgsman 1992;Wesslingh 1994; Harrison 2003]

Membrane separation

Membrane separation in this respect uses the difference in size between the water and the other components. Membrane separation can be micro-filtration, ultra-filtration or electrodialysis, depending on the type and size of the components to be separated. Membrane operations are discussed in appendix 1-13.

Purification

Elution chromatography

Chromatography is a kinetic separation. The technique is based on the affinity of the different species in the mixture to the adsorbent on the bed. The feed mixture is dissolved in a well-chosen solvent and then led over the chromatograph. The higher the affinity of a product for the adsorbent, the slower it will pass through the bed. Depending on the type of adsorbent, different mechanisms are responsible for the separation. The separation mechanism can be adsorption, ion-exchange, filtration, or affinity of the product. Adsorption is described in the previous section. Ion-exchange also effects a separation, because some components will remain in the bed longer, because of the different strengths of the electrostatic bonds. Filtration is based on the pore size in the bed. Smaller components can diffuse into the pores, which prolongs their residence time. When the affinity of the components for the bed are the main reason for separation, the Van der Waals forces are the main cause, and no real bonding takes place as in adsorption. [Belter 1988; Krijgsman 1992;Wesslingh 1994; Harrison 2003]

Precipitation

A typical characteristic in precipitation is the low concentrations of desired product in the mixture. Precipitation occurs when a component is added or the temperature is changed, which causes the solubility of the product to drop. This causes the product to precipitate. The precipitate can then be removed by centrifugation. This method is mostly used for the purification of proteins. [Belter 1988; Krijgsman 1992;Wesslingh 1994; Harrison 2003]

Ultra-filtration

Ultra-filtration and micro-filtration are membrane processes. The basis for separation is the same in conventional filtration, micro-filtration and ultra-filtration. In ultra-filtration the membrane is operated in a cross-flow mode. This eliminates the filter cake that is typical for normal filtration.

Formulation

Crystallisation

Crystallisation yields a very pure product, because during the process a lattice is formed, and the lattice does not allow for many impurities to be built in.
Crystallisation occurs when the solute concentration is increased above its saturation point. When the concentration becomes too high, nucleation takes place. This lowers the concentration of the solute in the solution. The nuclei will only grow to become crystals if the super-saturation remains. Crystallisation is en exothermic process so sufficient cooling is necessary. [Belter 1988; Krijgsman 1992;Wesslingh 1994 Harrison 2003]

Drying

Drying serves many purposes. The quality of the product can be defined in terms of moisture content because of product stability, or preservation of enzyme activity. On the other hand, recovery of expensive solvents is a strong economic incentive.
Simply boiling off the solvent cannot always be done, because the product might not be thermally stable at that temperature. Therefore alternative as freeze-drying, tumble-drying and spray drying have been developed. The drying is achieved by vacuum, kinetic and heat energy respectively. Sweep gases or vacuum increase the evaporation tendencies of the solvent. [Belter 1988; Krijgsman 1992;Wesslingh 1994 Harrison 2003]

Appendix 4-3: Solvent recovery

This appendix describes the different options that were conceived for the solvent recovery task. Solvent recovery was considered to be key to improving the DSP sub-process to achieve a truly sustainable design. Finally the design chosen is described.

Task options

Ultracentrifuge and molecular sieves

In this configuration, ultracentrifuge or ultracentrifugation would be used to separate off the cell debris, after which the mixture would be led through a molecular sieve, in order to separate water from the mixture. This configuration has many disadvantages. Not only are ultracentrifuge and ultra-filtration very expensive, the mixture has to be entirely free of cell debris, because otherwise the molecular sieve will be plugged by cell debris. Furthermore, two units are needed to effect the separation. This is not a preferable situation.

Heating

An option to facilitate the removal of the cell debris could be heating of the mixture. If the temperature is high enough, the proteins will denature, which decreases the solubility and alters the tertiary structure of the proteins dramatically. Disadvantages of heating are the energy intensity and the fact that it will always be necessary to use two units.

Distillation

Distillation would be another option to remove celan water from the system, by recovering t-butanol from the solvent waste stream. The mixture entering the column would however have to be free of cell debris, because the debris will deposit on the internals of the column, and thereby reducing the efficiency of the separation. Regular cleaning of the column is not a good option. For this option, also 2 units are necessary for the completion of the task.

Stripping

Stripping resembles the distillation option, with the difference that it is possible to perform a stripping operation without internals. Therefore it is possible to feed the contaminated mixture to the stripper. Moreover, communication with dr. Van der Lans (see appendix 8-3) revealed that particles prefer to be at a gas/liquid interface. Therefore the bubbles in the stripping column will transport the cell debris to the surface of the mixture. A clear water stream comes from the bottom, and the debris can be skimmed off at the top of the column. In this way only one unit is needed for the execution of the solvent recovery task.

Option chosen: Stripping with a random packed column

The option finally chosen for the solvent recovery step was stripping in a randomly packed column. Aspen showed that to achieve a high t-butanol efficiency at least 9 equilibrium stages would be needed. How this could be achieved in a bubble column is unclear as the degree of mixing would be likely to be too high. Given the time constraints a stripper was considered the best option. Calculations for the fermentation section had also demonstrated that calculations on bubble columns were complicated by pressure differentials and varying bubble diameters.

A packed column was chosen because the packing offers an enormous surface area over which cell debris can deposit. This is in contrast to a plate column where gas passes through a few narrow orifices on each plate, if these became blocked the column make behave in a very unpredictable way. In addition the column required was so narrow (0.3m diameter) that access to clean it was not possible. In contrast the internals of the random packed stripper could be removed, if that was required.

The smallest packing possible was chosen so as to ensure that vapour would not bypass the interior of the column due to a lower packing density at the column wall. In addition a smaller packing resulted in a wider, shorter column which was desirable to achieve a column with realistic proportions.

It was envisaged that the cell debris would precipitate within the column by forming a coating on the packing. Under normal operation this biofilm would eventually release locally and fall downward with the liquid stream. Over time an equilibrium would be established between the rate of precipitation and the rate of debris entrainment in the liquid flow. This is an assumption which would need to be tested at the lab scale.

If this did not happen a further option would be to take the column temporarily offline and pass hot gas from through the column, this would dry the debris and cause it to shrink and release.

In any case cell debris would leave the column at some point with the liquid water stream. It can then be recovered by centrifugation, filtration or using a scroll decanter depending on particle size and density.

Appendix 4-3: Solvent recovery

Appendix 4-4: Unit design in downstream processing

In this appendix the design of the various units used in the downstream sub-process is discussed. In total the design of 5 types of unit are discussed namely: centrifuges, the microfiltration unit, the stripper, homogenisers and the cyclone.

Centrifuge design (units S04, S05 and S07)

In centrifugation there are mainly three forces that play a role in the separation. The first is the buoyancy force, F_B. This force describes the frictionless acceleration of a spherical particle. However, the particle has to move through a solution, which yields a drag force resistance, F_D. Finally there is the inertial acceleration the particle experiences as a result of the centrifuges rotation. The equations for these forces are as follows:

$$F_B = \left[\frac{\pi d^3}{6}\left(\rho_s - \rho\right)\right] a$$

$$F_D = 3\pi d \mu v$$

F_B describes both the buoyant and inertial forces experienced by the particle. In these equations the nomenclature is the same as in the micro-filtration. ‘a’ Is the acceleration due to the applied force [m^2/s]. In centrifugation this force can be described by $a = \omega^2 r$. Here ω is the angular rotation [rad/s] and r is the distance of the particle from the centre of the centrifuge.
At steady-state the forces are in equilibrium, and the following equation for the velocity of the particle can be found:

$$v = \frac{d^2}{18\mu}\left(\rho_s - \rho\right)\omega^2 r$$

There are many different types of centrifuges. For simplicity we chose to compare three types of centrifuges. For the different types of centrifuges, the forces are applied in a different way. Nonetheless, the centrifuges can be described by similar means. Σ is a centrifuge-type dependent variable. Based on this variable a choice of centrifuge can be made.
A disk type centrifuge is the best option for the separation of cells, whereas a tubular centrifuge is usually used for the recovery of proteins. [Harrison 2003].
The ultimate design equation of a disk type centrifuge is as follows:

$$Q = \left\{\frac{2a^2\left(\rho - \rho_0\right)g}{9\mu}\right\}\left[\frac{2n\pi\ \omega^2\left(R_0^3 - R_1^3\right)\cot\theta}{3g}\right] = v_g \Sigma .$$

In this equation the symbols have the following descriptions:

Q	[kg/s]	Flow
a	[m]	diameter of the solute granule
ρ	[kg/m^3]	Density of the solute
ρ_0	[kg/m^3]	Density of the solvent
g	[m/s^2]	Gravitational acceleration
μ	[Pa·s]	Viscosity
n	[-]	Number of discs
ω	[rad/s]	Frequency of rotation
τ	[°]	Inclination of the plates
R_0	[m]	Inner radius
R_1	[m]	Outer radius

From this equation it is clear that Q and v_g are known. Therefore Σ is also known and the frequency of rotation for a given set of centrifuge dimensions can be determined. These calculations were performed for all three centrifuges individually.

Harrison [2003] also describes how the rate of sedimentation in a centrifuge decreases as the particle concentration increases, this is known as 'hindered settling'. To an extent this is compensated by the fact that for a give flow of particles a higher concentration results in a lower liquid flux through the centrifuge.

For this reason a sensitivity analysis was performed to determine over what ranges centrifugation is most efficient. The results are shown in Figure 0-1. This figure shows that the effective centrifuge efficiency increases up to a fraction mass fraction of 20% PHB granules (for a continuous mass flow of granules) before dropping away above a mass fraction of 60%.

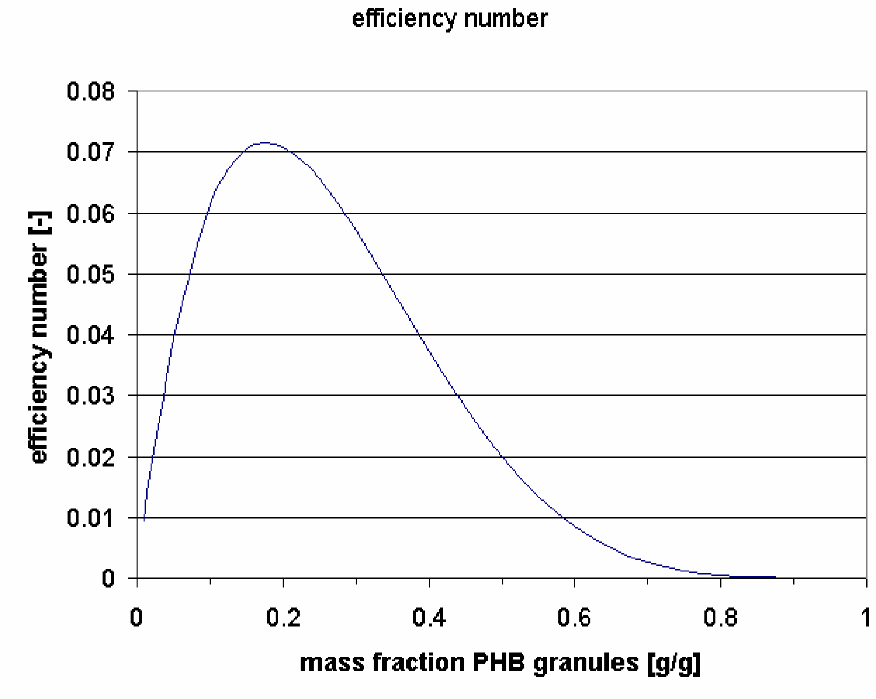


Figure 0-1: Efficiency of centifugation as a function of PHB mass fraction

It was also important to quantify the influence of the solids mass fraction on the relative settling velocity. This was calculated and the results are shown in Figure 0-2. This shows that even at a mass fraction of 15% the influence of other particles can reduce the rate of settling by 50%.

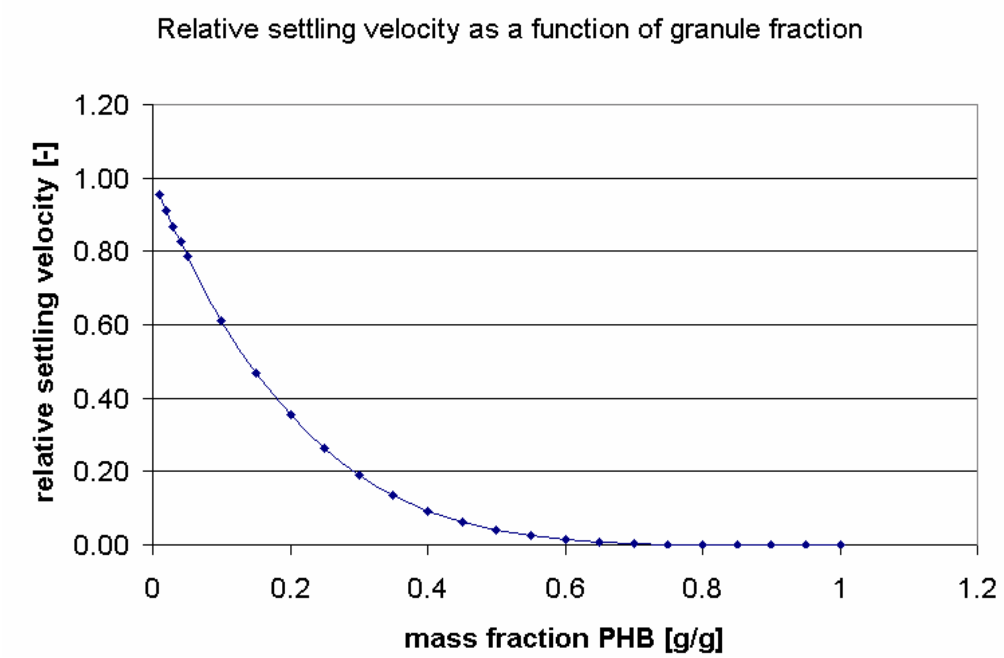


Figure 0-2: Relative particle settling velocity

In each case the quality of the separation was excellent for the smallest continuous centrifuge listed by Harrison [2003]. This resulted in frequencies of 3000, 2250 and 2250 for centrifuges S04, S05 and S06 respectively. The maximum rate of rotation these units can achieve is 10000 rpm, so there remains some overcapacity in the centrifuges. However given the effect of hindered settling this overcapacity may not be as significant as it appears.

Micro-filtration design (unit S03)

The flux through the membrane can be described as follows:

$$N = \frac{P_m}{l_m}\left(P_0 - P_l\right)$$

P_m is the permeability of the membrane [s], l_m [m] is the membrane thickness, and $P_0 - P_l$ [Pa] is the driving force over the membrane.

The permeability can be described by the following equation.

$$P_m = \frac{\varepsilon \rho D^2}{32\mu}$$

The pore diameter is symbolised by D [m], ε is the membrane porosity [-]. ρ symbolises the density of the fluid [kg/m^3], μ symbolises the viscosity of the fluid [Pa·s]. These equations assume bulk flow in a porous membrane with straight pores.

Stripper design (unit C01)

The stripper was designed using a combination of Aspen and sulpak. These are two calculation programs. Aspen is a flowsheeting application which is used to provide information on the thermodynamics of the stripper design. Sulpak is a program used to calculate the performance of a packed column.

Initially aspen was used to calculate the number of equilibrium stages required and the properties of the mass streams. Sulpak was then used to dimension the column and calculate the pressure drop over the column. The pressure drop found was then used to recalculate in Aspen, this process resulted in convergence between the two programs in two iterations.

These final column dimensions, calculated using sulpak, are as follows:

Sulpak Column Data Sheet

	Unit		
Bed		1	
Diameter	m	0.31	
Packing Type		NR1	
Material		1.0330 (DIN)	
NTS		9	
NTSM expected		2	
Height	m	4.5	
Foam factor		1	
Liquid holdup	%	5.66374	
Pressure drop	mbar	14.53331	
		Top	Bottom
Gas load	kg/h	663	265
Liquid load	kg/h	1635	1236
Gas density	kg/m^3	1.62	0.39
Liquid density	kg/m^3	860.9	918
Surface tension	mN/m	72.8	72.8
Liquid viscosity	cP	1.2	1.2
Gas viscosity	cP	0.02	0.02
Capacity	%	79.44	61.09922
F-Factor	Pa^0.5	1.91708	1.561701
Spec. liquid load	m^3/m^2*h	25.16238	17.83867
dp/dz	mbar/m	4.25164	2.20761

Figure 0-3: Column dimension from sulpak

Homogeniser design (units A02 and A03)

The homogenisers were dimensioned primarily using literature values. The efficiency of the homogenisers is not something which can be meaningfully calculated from first principles. It will depend on the viscosity of the mixture, the fluid dynamics in the valve and the thickness of the bacterial cell wall. None of those parameters can be accurately predicted, especially as the very process of homogenisation will alter the viscosity. For this reason the extensive experimental values determined by Ghatnekar [2001] were used to determine optimal operating conditions.

To calculate the duty of the pump and the change in temperature of the liquids Aspen was used. The homogenisers were simulated using a pump followed by a valve. This was extremely useful in determining the likely temperature rise, this can not be too high or else cell debris will not solvate. In addition t-butanol vapour will form if the temperature is too high, which can lead to cavitation in the homogenisers.

Cyclone design (unit S06)

Cyclone design was one of the last issues addressed in the development of the downstream subprocess. Discussion with experts provided the group with the knowledge that polymer particles become charged and will tend to agglomerate. This makes the use of a cyclone possible. However it did not provide a means to determine the rate of charging or the rate of agglomeration, both of which are necessary to estimate the size of the agglomerates which are to be collected. For this reason a conservative estimate had to be made. This was taken to be agglomerates with a diameter of 1.2 microns. This is equivalent to PHB granules agglomerating in groups of about 4 particles. With this information a cyclone system for dry product recovery was calculated.

Appendix 5:
Equipment Specification sheets

STORAGE TANK - SPECIFICATION SHEET

EQUIPMENT NUMBER		T01	
NAME		Sand storage hopper	
General Data			
Service			Sand storage
Type			Solids hopper
Position			Vertical
Volume	**[m3]**		10.00
Diameter	**[m]**		1.40
Length	**[m]**		6.50
thickness wall	**[mm]**		12.0
solids volume	**[m3]**		7.00
solids height	**[m]**		4.55
Maximum load	**[kg]**		26000

Remarks:

material of construcion: CS (carbon steel)

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

STORAGE TANK - SPECIFICATION SHEET

EQUIPMENT NUMBER	T02	
NAME	Wood feedstock storage	
General Data		
Service		Feedstock storage
Type		Warehouse
Position		-
Volume	**[m3]**	22500.00
Height	**[m]**	7.50
Length	**[m]**	100.00
Width	**[m]**	30.0
Density stored material	**[kg/m3]**	750.0
target load	**[kg]**	6200000
Maximum load	**[kg]**	8437500

Remarks:

material of construcion: CS (carbon steel)

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

STORAGE TANK - SPECIFICATION SHEET

EQUIPMENT NUMBER		T03
NAME		DSP solvent storage
General Data		
Service		Solvent storage
Type		Atmospheric liquid storage
Position		Vertical
Volume	**[m3]**	2.46
Diameter	**[m]**	1.00
Length	**[m]**	3.13
thickness wall	**[mm]**	5.0
liquid volume	**[m3]**	1.72
liquid height	**[m]**	2.19
Maximum load	**[kg]**	2455

Remarks:

material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

MILL - SPECIFICATION SHEET

EQUIPMENT NUMBER		A01	
NAME		Crusher	
General Data			
Service		milling wood chips	
Type		Hammermill	
Power	**[hp]**	250	
Capacity	**[t/hr]**	6	
Diameter	**[m]**	3	
Length	**[m]**	4	
Speed	**[rpm]**	1800	
Screen sizes	**[mm]**	3.18--4.76-6.34	1/8" - 3/16" - 1/4"
hammer thickness	**[mm]**	12.68	1/2"
number of hammers	**[m]**	88	
diameter hammers extended	**[m]**	0.66	
feed surface	**[m*m]**	1.5*1	

Process Conditions

Stream Details		**Feed**		**Out**	
Temp.	**[°C]**	20		20	
Pressure	**[bara]**	1		1	
Density	**[kg/m^3]**	750		750	
Mass Flow	**[kg/s]**	1550		1550	
PSD	**[mm]**	30		5	
Composition		**mol%**	**wt%**	**wt%**	**mol%**
wood		100	100	100	100

Remarks:
The PSD (particle size distribution) gives the average surface-volume particle size

Designers	L.M.A.W. Franssen	Project ID-Number	CPD3310
		Date	18/07/2004

HOMOGENISER - SPECIFICATION SHEET

EQUIPMENT NUMBER		A02
NAME		Broth homogeniser #1

General Data

Service		Homogenisation
Type		Gaulin homogeniser
Position		horizontal
Valve type		ceramic
Pump type		reciprocal
Pressure drop	**[bara]**	399
Pump power	**[kW]**	6.47

Process Conditions

Stream Details		**Feed**	**Output**	
Temp.	**[^oC]**	70.8	73.9	
Pressure	**[bara]**	1.00	1.00	
Density	**[kg/m^3]**	869	865	
Mass Flow	**[kg/s]**	0.525	0.525	
Viscosity	**[PaS]**	1.20E-03	1.20E-03	

Composition	**mol%**	**wt%**	**mol%**	**wt%**		
water	88.8	59.8	88.8	59.8		
t-butanol	11.2	31.0	11.2	31.0		
PHB		6.9		6.9		
Debris		2.3		2.3		

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	22/07/2004

HOMOGENISER - SPECIFICATION SHEET

EQUIPMENT NUMBER	A03
NAME	Broth homogeniser #2

General Data

Service		Homogenisation
Type		Gaulin homogeniser
Position		horizontal
Valve type		ceramic
Pump type		reciprocal
Pressure drop	**[bara]**	399
Pump power	**[kW]**	6.50

Process Conditions

Stream Details		**Feed**	**Output**	
Temp.	**[^{o}C]**	73.9	77.1	
Pressure	**[bara]**	1	1	
Density	**[kg/m^3]**	865	861	
Mass Flow	**[kg/s]**	0.525	0.525	
Viscosity	**[PaS]**	1.20E-03	1.20E-03	

Composition	**mol%**	**wt%**	**mol%**	**wt%**		
water	88.8	59.8	88.8	59.8		
t-butanol	11.2	31.0	11.2	31.0		
PHB		6.9		6.9		
Debris		2.3		2.3		

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	22/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S01
NAME		syngas cleanup
General Data		
Service		Solids removal
Type		High Efficiency Cyclone
Number of cyclones		1
Pressure drop	**[bara]**	
Efficiency	**[-]**	0.900
Cyclone dimensions		
D	**[m]**	1.035
De	**[m]**	0.517
Dd	**[m]**	0.388
Lb	**[m]**	1.552
Lc	**[m]**	2.586
H	**[m]**	0.517
W	**[m]**	0.207
S	**[m]**	0.517

Process Conditions

Stream Details		**Feed**	**Gas out**	**Solids**
Temp.	**[^{o}C]**	884	884	884
Pressure	**[bara]**	5.00	5.00	5.00
Density	**[kg/m^3]**	1.15	1.15	2600
Mass Flow	**[kg/s]**	1.6	1.6	1.46E-04
Volumetric flow	**[m3/s]**	1.391	1.391	5.62E-08
Composition		**wt%**	**wt%**	**wt%**
Gases		99.999	100	
Solids		0.001		100

Remarks:
Construction material SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	29/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S02
NAME		syngas filter
	General Data	
Service		Gas cleanup
Type		Ceramic filter
Operation mode		Swing
Number of filters		2
Pressure drop	**[bara]**	0.030
Filter dimensions		
Area	**[m2]**	92.9
Pore size	**[m]**	5.00E-07
Efficiency	**[-]**	0.999
Cycle time	**[hours]**	1000
Floor space required	**[m2]**	6.80
Gas velocity	**[m/s]**	0.015

Process Conditions

Stream Details		**Feed**	**Gas out**	**Solids**
Temp.	**[^oC]**	883.55	883.55	883.55
Pressure	**[bara]**	5.00	5.00	5.00
Density	**[kg/m^3]**	1.15	1.14	2000
Mass Flow	**[kg/s]**	1.595	1.595	0.051
Volumetric flow	**[m3/s]**	1.387	1.399	2.550E-05
Composition		**wt%**	**wt%**	**wt%**
Gases		0.999	1	0
Solids		0.001	0	1

Remarks:
The filter is a ceraminc monolith.

Designers	R. Toonssen	Project ID-Number	CPD3310
		Date	28/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S03
NAME		Broth concentrator
	General Data	
Service		Product concentration
Type		Microfiltration unit
Position		Horizontal
Membrane area required	**[m^2]**	0.921
Fiber Diameter	**[m]**	0.001
Fiber Length	**[m]**	0.800
Fiber area	**[m^2]**	2.51E-03
Pore Diameter	**[m]**	3.00E-06
Pore Density	**[m^{-2}]**	4.00E+09
Fibers per bundle		100
Bundles		4
Housing construction Material		Polypropylene
Fiber material		Polyester
Vessel volume		0.00100531

Process Conditions

Stream Details		**Feed**		**Retentate**		**Permeate**	
Temp.	**[^oC]**	40.0		40.0		40.0	
Pressure	**[bara]**	5.00		4.50		1.00	
Density	**[kg/m^3]**	979		979		979	
Mass Flow	**[kg/s]**	0.477		0.112		0.365	
Viscosity	**[PaS]**	1.20E-03		1.20E-03		1.20E-03	
Composition		**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water		100	89.9	1	57.5	100	99.9
t-butanol		0.00	0.00	0.00	0.00	0.00	0.00
PHB			7.57		31.9		0.10
Debris			2.50		10.6		0.01

Remarks:

Designers	D. Richheimer	Project ID-Number	CPD3310
		Date	18/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S04
NAME		Raw PHB recovery
General Data		
Service		Product concentration
Type		Disk Centrifuge
Centrifuge Diameter	**[m]**	0.254
Rotation Frequency	**[Hz]**	3000
Disk count		4
Disk inclination	**[rad]**	0.698
Sigma Requirement	**[m^2]**	1.48E+04

Process Conditions

Stream Details		**Feed**		**Clarified liquid**		**Sediment**	
Temp.	**[^oC]**	77.13		77.13		77.13	
Pressure	**[bara]**	1.00		1.00		1.00	
Density	**[kg/m^3]**	947		1814		882	
Mass Flow	**[kg/s]**	0.525		0.07		0.454	
Viscosity	**[PaS]**	1.20E-03		1.20E-03		1.20E-03	
Composition		**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water		88.8	59.8	88.8	31.2	88.8	64.2
t-butanol		11.2	31	11.2	16.2	11.2	33.3
PHB			6.9		50.9		0.1
Debris			2.3		1.7		2.3

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	18/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S05
NAME		pure PHB recovery (wet)
General Data		
Service		Product concentration
Type		Disk Centrifuge
Centrifuge Diameter	**[m]**	0.254
Rotation Frequency	**[Hz]**	2250
Disk count	**[m^{-2}]**	4
Disk inclination	**[rad]**	0.698
Sigma Requirement	**[m^2]**	6.67E+03

Process Conditions

Stream Details		**Feed**		**Clarified liquid**		**Sediment**	
Temp.	**[°C]**	71.7		71.7		71.7	
Pressure	**[bara]**	1.00		1.00		1.00	
Density	**[kg/m^3]**	786		786		786	
Mass Flow	**[kg/s]**	0.271		0.218		0.053	
Viscosity	**[PaS]**	1.20E-03		1.20E-03		1.20E-03	
Composition		**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water		58.1	21.8	58.1	25.2	58.1	7.8
t-butanol		41.9	64.6	41.9	74.6	41.9	23.1
PHB			13.2		0.2		66.8
Debris			0.4		0		2.2

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	18/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER	S06
NAME	pure PHB recovery (dry)

General Data

Service		Product concentration
Type		High Efficiency Cyclone - array
Array connectivity		parallel
Number of cyclones		3
Pressure drop	**[bara]**	0.090
Cyclone dimensions		
D	**[m]**	0.090
De	**[m]**	0.045
Dd	**[m]**	0.022
Lb	**[m]**	0.179
Lc	**[m]**	0.179
H	**[m]**	0.045
W	**[m]**	0.022
S	**[m]**	0.011

Process Conditions

Stream Details		**Feed**	**Gas out**	**Solids**
Temp.	**[^{o}C]**	85.1	82.6	82.6
Pressure	**[bara]**	1.10	1.00	1.00
Density	**[kg/m^3]**	1.75	1.61	1250
Mass Flow	**[kg/s]**	0.237	0.201	0.0366
Volumetric flow	**[m3/s]**	0.135	0.125	2.925E-05
Viscosity	**[PaS]**	1.50E-05	1.50E-05	-

Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water	48.3	15.6	48.3	16.9		0
t-butanol	51.7	69.0	51.7	74.7		0
PHB		15.0		8.1		96.8
Debris		0.4		0.3		3.2

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	18/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		S07
NAME		Debris removal
	General Data	
Service		Liquid purification
Type		Stacked Disk Centrifuge
Centrifuge Diameter	**[m]**	0.254
Rotation Frequency	**[Hz]**	2250
Disk count	**[m^{-2}]**	4
Disk inclination	**[rad]**	0.698
Sigma Requirement	**[m^2]**	6.85E+03

Process Conditions

Stream Details		**Feed**		**Clarified liquid**		**Sediment**	
Temp.	**[^{o}C]**	99.8		99.8		99.8	
Pressure	**[bara]**	1.00		1.00		1.00	
Density	**[kg/m^3]**	918		918		918	
Mass Flow	**[kg/s]**	0.343		0.321		0.022	
Viscosity	**[PaS]**	1.20E-03		1.20E-03		1.20E-03	
Composition		**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water		100	96.8	100	100	100	49.9
t-butanol		0	0	0	0	0	0
PHB			0.1		0		1.6
Debris			3.1		0		48.5

Remarks:

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	18/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER	VO1	
NAME	Wood hopper	
General Data		
Service		Solvent buffering/storage
Type		Column vessel
Position		Vertical
Volume	**[m3]**	5.00
Diameter	**[m]**	1.25
Length	**[m]**	4.07
thickness wall	**[mm]**	5.0
Maximum load	**[kg]**	3750
Density medium	**[kg/m3]**	750

Remarks:

material of
construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		V02	
NAME		Pressurised Hopper	
General Data			
Service		Solvent buffering/storage	
Type		Column vessel	
Position		Vertical	
Volume	**[m3]**		5.00
Diameter	**[m]**		1.25
Length	**[m]**		4.07
thickness wall	**[mm]**		5.0
Maximum load	**[kg]**		3750
Density medium	**[kg/m3]**		750

Remarks:

material of
construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

SEPARATION UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		V03
NAME		Gas-liquid separator

General Data

Service		water removal from syn-gas
Type		knock-out drum
Position		Horizontal
Volume	**[m3]**	1
Diameter	**[m]**	0.75
Length	**[m]**	2.25
thickness wall	**[mm]**	5
efficiency	**[%]**	>99
liquid volume holdup	**[m3]**	0.49
liquid height holdup	**[m]**	0.38
fv (part area for vapour)	**[-]**	0.5
holdup time	**[min]**	15

Process Conditions

Stream Details		**Feed liquid**	**Feed gas**	**gas out**	**water out**
Temp.	**[^{o}C]**	40	40	40	40
Pressure	**[bara]**	5	5	5	5
Density	**[kg/m^3]**	992.391	5	5	992.391
Mass Flow	**[kg/s]**	1895	3847	3847	1895

Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
hydrogen	0.136	0.27192	0.00	0.00	0.22	0.45
methane	0	0	0.00	0.00	0.00	0.00
water	0.39874	7.17732	0.99	17.82	0.01	0.26
CO	0.10436	2.92208	0.00	0.02	0.17	4.81
CO2	0.079687	3.506228	0.01	0.32	0.13	5.58
O2	0	0	0.00	0.00	0.00	0.00
N2	0.28118	7.87304	0.00	0.06	0.46	12.95
H2S	0.000059154	0.002011236	0.00	0.00	0.00	0.00
NO	4.6117E-07	1.38351E-05	0.00	0.00	0.00	0.00
NO2	0	0	0.00	0.00	0.00	0.00
HCl	0.000012849	0.000468989	0.00	0.00	0.00	0.00
NH3	0.000003933	0.000066861	0.00	0.00	0.00	0.00

Remarks:
material of construcion: SS 18/8

Designers	L.M.A.W. Franssen	Project ID-Number	CPD3310
		Date	18/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		V04
NAME		Recycle water vessel
	General Data	
Service		Solvent buffering/storage
Type		Column vessel
Position		Vertical
Volume	**[m3]**	5.00
Diameter	**[m]**	1.25
Length	**[m]**	4.07
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	3.50
liquid height holdup	**[m]**	2.85
Maximum load	**[kg]**	5000
Density medium	**[kg/m3]**	1000

Remarks:

material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		V05
NAME		nutrient solution/storage vessel
General Data		
Service		Solvent buffering/storage
Type		Column vessel
Position		Vertical
Volume	**[m3]**	5.00
Diameter	**[m]**	1.25
Length	**[m]**	4.07
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	3.50
liquid height holdup	**[m]**	2.85
Maximum load	**[kg]**	5000
Density medium	**[kg/m3]**	1000

Remarks:

material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		V06
NAME		solvent buffer/storage vessel
	General Data	
Service		Solvent buffering/storage
Type		Column vessel
Position		Vertical
Volume	**[m3]**	5.00
Diameter	**[m]**	1.25
Length	**[m]**	4.07
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	3.50
liquid height holdup	**[m]**	2.85
Maximum load	**[kg]**	4500
Density medium	**[kg/m3]**	900

Remarks:

material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

VESSEL UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER	V07	
NAME	Hydrogen storage vessel	
General Data		
Service		Solvent buffering/storage
Type		Column vessel
Position		Vertical
Volume	**[m3]**	5.00
Diameter	**[m]**	1.25
Length	**[m]**	4.07
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	3.50
liquid height holdup	**[m]**	2.85
Maximum load	**[kg]**	4500
Density medium	**[kg/m3]**	900

Remarks:

material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

EQUIPMENT NUMBER	K01	**Operating**	1
NAME	R01-Methane	**Installed spare**	1
Service	Gasification methane feed		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped fluid	Methane		
Temperature (T) [ºC]	398.55		
Density (r) [kg/m^3]	0.55		
Viscosity (h) [$N \cdot s/m_2$]			
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f_v) [m^3/s]	0.07		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5		
Theoretical power [kW]	29.6		
Pump efficiency [-]	0.3		
Power at shaft [kW]	98.6666667		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v / p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	K02	**Operating**	1
NAME	R01 feed	**Installed spare**	1
Service	Gasification air supply		
Type	Two stage turbo Compressor		
Number	1		
Operating Conditions & Physical Data			
Pumped liquid	Air		
Temperature (T) [ºC]	398.55		
Density (r) [kg/m^3]	2.61324042		
Power			
Capacity (f$_v$) [m^3/s]	0.64		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5		
Theoretical power [kW]	182.59		
Pump efficiency [-]	0.72		
Power at shaft [kW]	253.597222		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	K03	**Operating**	1
NAME	R01-steam	**Installed spare**	1
Service	Gasification steam supply		
Type	Two stage turbocompressor		
Number	1		
Operating Conditions & Physical Data			
Pumped liquid	Steam		
Temperature (T) [ºC]	360		
Density (ρ) [kg/m^3]	0.351		
Power			
Capacity (ϕ_v) [m^3/s]	1.189		
Suction pressure (p_s) [bar]	5		
Discharge pressure (p_d) [bar]	10		
Theoretical power [kW]	323.27		
Pump efficiency [-]	0.72		
Power at shaft [kW]	448.986111		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	K04	**Operating**	1
NAME	R02 feed	**Installed spare**	1
Service	Syn-gas feed		
Type	Two stage turbocompressor		
Number	1		
Operating Conditions & Physical Data			
Pumped liquid	Syn-gas		
Temperature (T) [ºC]	40		
Density (r) [kg/m^3]	0.0011		
Power			
Capacity (f$_v$) [m^3/s]	0.228		
Suction pressure (p_s) [bar]	5		
Discharge pressure (p_d) [bar]	5.5		
Theoretical power [kW]	15.5		
Pump efficiency [-]	0.72		
Power at shaft [kW]	21.5277778		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	K05	**Operating**	1
NAME	S06 feed	**Installed spare**	1
Service			
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/t-butanol mixture		
Temperature (T) [ºC]	99		
Density (r) [kg/m^3]	969		
Power			
Capacity (f_v) [m^3/s]	0.10		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	5.19		
Pump efficiency [-]	0.72		
Power at shaft [kW]	7.21412037		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

REACTOR - SPECIFICATION SHEET

EQUIPMENT NUMBER	R01		
NAME	Fluidised Bed Reactor/Gasifier		

General Data

Service	reaction/gasification			
Reactor Type	fluidised bed			
Bed height [m]		3	**bed diameter [m]**	1.2
Freeboard height [m]		5	**Freeboard diameter [m]**	1.5
Bed filling	river sand		**wall thickness [mm]**	12
Bed porosity [-]		0.4		
Bed particle diameter [mm]		0.5		
Total Volume		12		
Reactor Diameter [m]		1.2-1.5	**Column material**	SS 321
Total Height [m]		8	**mass sand [kg]**	5429
Heating	none			

Process Conditions

Stream Details	**Feed solid**		**Feed gas**		**Exit top**		**Bottom**	
Temp. [^{o}C]	25		1173		1537		1300	
Pressure [bara]	5		5		5		5	
Density [kg/m^3]	750		0.92		0.85		1.2	
Mass Flow [kg/h]	1551		4200		5742		8.0000	
Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
wood		99.9						
water			0.47	0.357	39.650	32.93		
H2					14.24	1.32		
methane					0.00	0.00		
CO					9.69	12.51		
CO2					8.44	17.12		
O2			0.11	0.150	0.00	0.00		
N2			0.42	0.493	27.97	36.11		
H2S					0.01	0.01		
HCl					0.00	0.00		
NO					0.00	0.00		
NO2					0.00	0.00		
ammonia					0.00	0.00		
ash								87.8
sand		0.1						12.2

Column Internals *(4)*

Packing	none			
Filling	river sand		SV-diameter	0.5 mm
grid	area (m^2)			1.13
gas distributor	perforated plate	area (m^2):		1.13
Material	SS 321			
Width [m]		1.20		
Height [m]		0.01		

Remarks:

(1) SS = Stainless Steel

(2) Reactor diameter changes at 3m height from 1.2m to 2m width - for freeboard

Designers	Project ID-Number	CPD3310
LMAW Franssen	Date	18/07/04

Membrane bio-Fermentation Reactor - SPECIFICATION SHEET

EQUIPMENT NUMBER	R02
NAME	Growth Reactor

General Data

Service	Growth of biomass		
Reactor Type	Bubble column with mebranes	**Reactor material**	SS 18/8
Volume Reactor [m^3]	8	Wall thickness [mm]	7
Reactor Height [m]	3	Int. pressure [bar]	5
Reactor Diameter [m]	1.5	Int. temperature [^oC]	40
Membrane type	Dense hollow fiber membrane	**Membrane material**	Silicone Rubber
Heat exchanger type	Dimpel cooling jacket	**Cooling jacket material**	SS 18/8
cooling medium	water		
Exchange suface [m^2]	5		
Aerator	sparger	**Sparger material**	SS 18/8

Process Conditions

Stream Details	**Liquid Feed**	**Synthesis gas feed**	**Air feed**	**Liquid out**	**Synthesis gas out**	**Air out**
Temp. [^oC]	20	40	20	40	40	40
Pressure [bara]	5.0	10.0	5.3	5.0	10.0	5.0
Density [kg/m^3]	1,000.0	9.6	6.3	1,000.0	12.6	5.5
Mass Flow [kg/s]	0.24	0.26	0.89	0.26	0.25	0.60

Composition	**Liquid Feed mol%**	**Liquid Feed wt%**	**Synthesis gas feed mol%**	**Synthesis gas feed wt%**	**Air feed mol%**	**Air feed wt%**	**Liquid out mol%**	**Liquid out wt%**	**Synthesis gas out mol%**	**Synthesis gas out wt%**	**Air out mol%**	**Air out wt%**
Water	100	100					97	95			2	0
Biomass							3	5				
H2			21	2					5	0		
CO			17	19					8	8		
CO2			13	23			0	0	25	35		
N2			49	56	79	77			61	57	80	79
O2					21	23					18	21
PHB							0	0				

Auxiliary reactor equipment *(4)*

Membrane		**Sparger**		**Heat Exchanger**	
Type	Dense	**type**		**Type**	Dimpel Cooling Jacket
Material	SS 18/8	**material**	SS 18/8	**Material**	SS 18/8
hold up [-]	0.50	**gas hold-up**	0.3	**Cooling medium**	Water
Length [m]	3.50	**Orifice**		**Exchange area [m^2]**	5.3
diameter [mm]	1.51			**Medium temp.in [C]**	15
Number of membranes	350,000			**medium flowrate [l/min]**	1.7
Exchange area [m^2]	5112				

Remarks:
Membranes are orientated along the axis of the column

Designers	R. Eijsberg M.J. ter Meulen	Project ID-Number	CPD3310
		Date	18/07/2004

Membrane bio-Fermentation Reactor - SPECIFICATION SHEET

EQUIPMENT NUMBER	R03
NAME	PHB production reactor

General Data

Service	Reaction		
Reactor Type	Bubble column with membranes	Reactor material	SS 18/8
Reactor Height [m]	3.4	Internal pressure [bar]	5
Reactor Diameter [m]	1.7	internal temperatur [C]	40
Membrane type	Dense hollow fiber membrane	**Membrane material**	Silicone Rubber
Number of mebranes	660,000		
Heat exchanger type	Dimpel Cooling jacket	**Cooling jacket material**	SS 18/8
cooling medium	water		
Exchange suface [m^2]	5		
Aerator	sparger	**Sparger material**	SS 18/8

Process Conditions

Stream Details	**Liquid Feed**		**Synthesis gas feed**		**Air feed**		**Liquid out**		**Synthesis gas out**		**Air out**	
Temp. [°C]	40		40		20		40		40		40	
Pressure [bara]	5.0		10.0		5.3		5.0		10.0		5.0	
Density [kg/m^3]	1,000.0		9.6		6.3		1,000.0		12.6		5.5	
Mass Flow [kg/s]	0.26		0.26		0.59		0.27		0.25		0.60	
Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
Water	97	95					96	91			0	0
Biomass	3	5					3	5				
H2			21	2					1	0		
CO			17	19					4	3		
CO2			13	23			0	0	30	40		
N2			49	56	79	77			66	57	81	79
O2					21	23					19	21
PHB							1	5				

Auxiliary reactor equipment *(4)*

Membrane		**Sparger**		**Heat Exchanger**	
Type	Dense	**type**		**Type**	Dimpel Cooling Jacket
Material	Silicon Rubber	**material**	stainless steel	**Material**	Stainless Steel
hold up [-]	0.50	**gas hold-up**	0.2	**Cooling medium**	Water
Length [m]	3.50	**Orifice**		**Exchange area [m^2]**	5.3
diameter [mm]	1.51			**Medium temp.in [C]**	15
Number of membranes	660,000			**medium flowrate [l/min]**	1
Exchange area [m^2]	10953				

Remarks:

Membranes are orientated along the axis of the column

Designers	R. Eijsberg M.J. ter Meulen	Project ID-Number	CPD3310
		Date	18/07/2004

Membrane bio-Fermentation Reactor - SPECIFICATION SHEET

EQUIPMENT NUMBER	R04
NAME	PHB production reactor

General Data

Service	Reaction		
Reactor Type	Bubble column with membranes	Reactor material	SS 18/8
Reactor Height [m]	3.4	Internal pressure [bar]	5
Reactor Diameter [m]	1.7	internal temperature[^{o}C]	40
Membrane type	Dense hollow fiber membrane	**Membrane material**	Silicone Rubber
Number of membranes	660,000		
Heat exchanger type	Dimpel Cooling jacket	**Cooling jacket material**	SS 18/8
cooling medium	water		
Exchange suface [m^2]	5		
Aerator	sparger	**Sparger material**	SS 18/8

Process Conditions

Stream Details	**Liquid Feed**		**Synthesis gas feed**		**Air feed**		**Liquid out**		**Synthesis gas out**		**Air out**	
Temp. [^{o}C]	40		40		20		40		40		40	
Pressure [bara]	5.0		10.0		5.3		5.0		10.0		5.0	
Density [kg/m^3]	1,000.0		9.6		6.3		1,000.0		12.6		5.5	
Mass Flow [kg/s]	0.27		0.26		0.59		0.28		0.25		0.60	
Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
Water	96	90					95	87			0	0
Biomass	3	5					3	4				
H2			21	2					1	0		
CO			17	19					4	3		
CO2	0	0	13	23			0	0	30	40		
N2			49	56	79	77			66	57	81	79
O2					21	23					19	21
PHB	1	5					2	9				

Auxiliary reactor equipment *(4)*

Membrane		**Sparger**		**Heat Exchanger**	
Type	Dense	**type**		**Type**	Dimpel Cooling Jacket
Material	Silicon Rubber	**material**	stainless steel	**Material**	Stainless Steel
hold up [-]	0.50	**gas hold-up**	0.2	**Cooling medium**	Water
Length [m]	3.50	**Orifice**		**Exchange area [m^2]**	5.3
diameter [mm]	1.51			**Medium temp.in [C]**	15
Number of membranes	660,000			**medium flowrate [l/min]**	1
Exchange area [m^2]	10953				

Remarks:
Membranes are orientated along the axis of the column

Designers	R. Eijsberg M.J. ter Meulen	Project ID-Number	CPD3310
		Date	18/07/2004

Membrane bio-Fermentation Reactor - SPECIFICATION SHEET

EQUIPMENT NUMBER	R05
NAME	PHB production reactor

General Data

Service	Reaction		
Reactor Type	Bubble column with membranes	Reactor material	SS 18/8
Reactor Height [m]	3.4	Internal pressure [bar]	5
Reactor Diameter [m]	1.7	internal temperatur [C]	40
Membrane type	Dense hollow fiber membrane	**Membrane material**	Silicone Rubber
Number of mebranes	660,000		
Heat exchanger type	Dimpel Cooling jacket	**Cooling jacket material**	SS 18/8
cooling medium	water		
Exchange suface [m^2]	5		
Aerator	sparger	**Sparger material**	SS 18/8

Process Conditions

Stream Details	**Liquid Feed**		**Synthesis gas feed**		**Air feed**		**Liquid out**		**Synthesis gas out**		**Air out**	
Temp. [°C]	40		40		20		40		40		40	
Pressure [bara]	5.0		10.0		5.3		5.0		10.0		5.0	
Density [kg/m^3]	1,000.0		9.6		6.3		1,000.0		12.6		5.5	
Mass Flow [kg/s]	0.28		0.26		0.59		0.29		0.25		0.60	
Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
Water	95	86					94	83			0	0
Biomass	3	5					3	4				
H2			21	2					1	0		
CO			17	19					4	3		
CO2	0	0	13	23			0	0	30	40		
N2			49	56	79	77			66	57	81	79
O2					21	23					19	21
PHB	2	9					3	13				

Auxiliary reactor equipment *(4)*

Membrane		**Sparger**		**Heat Exchanger**	
Type	Dense	**type**		**Type**	Dimpel Cooling Jacket
Material	Silicon Rubber	**material**	stainless steel	**Material**	Stainless Steel
hold up [-]	0.50	**gas hold-up**	0.2	**Cooling medium**	Water
Length [m]	3.50	**Orifice**		**Exchange area [m2]**	5.3
diameter [mm]	1.51			**Medium temp.in [C]**	15
Number of membranes	660,000			**medium flowrate [l/min]**	1
Exchange area [m^2]	10953				

Remarks:

Membranes are orientated along the axis of the column

Designers	R. Eijsberg M.J. ter Meulen	Project ID-Number	CPD3310
		Date	18/07/2004

EQUIPMENT NUMBER	P01	**Operating**	1
NAME	Water feed	**Installed spare**	1
Service	Water transfer pump		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water		
Temperature (T) [ºC]	25		
Density (r) [kg/m^3]	997		
Viscosity (h) [$N \cdot s/m_2$]	0.001		
Vapour pressure (p_v) [bar]	0.0233932	**at Temperature [ºC]**	20
Power			
Capacity (f_v) [m^3/s]	5.59E-05		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5		
Theoretical power [kW]	0.02236		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.07453333		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	978.1
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P02	**Operating**	1
NAME	Water feed fe	**Installed spare**	1
Service	Water transfer pump		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water		
Temperature (T) [ºC]	25		
Density (r) $[kg/m^3]$	997		
Viscosity (h) $[N \cdot s/m_2]$	0.001		
Vapour pressure (p_v) [bar]	0.0233932	**at Temperature [ºC]**	20
Power			
Capacity (f_v) $[m^3/s]$	5.59E-05		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5		
Theoretical power [kW]	0.02236		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.07453333		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	978.1
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P03	**Operating**	1
NAME	R02 feed	**Installed spare**	1
Service	Nutrient mixture inflow pump		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/Nutrients mixture		
Temperature (T) [ºC]	37		
Density (r) [kg/m^3]	997		
Viscosity (h) [$N^{\cdot} s/m_2$]	0.001		
Vapour pressure (p_v) [bar]	0.0233932	**at Temperature [ºC]**	20
Power			
Capacity (f$_v$) [m^3/s]	0.000235		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5		
Theoretical power [kW]	0.094		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.31333333		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	978.1
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P04	**Operating**	1
NAME	R05 effluent	**Installed spare**	1
Service	Fermentor broth		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water and bacteria		
Temperature (T) [ºC]	40		
Density (r) [kg/m^3]	**1030**		
Viscosity (h) [$N^{\cdot} s/m_2$]	0.001		
Vapour pressure (p_v) [bar]	0.0233932	**at Temperature [ºC]**	20
Power			
Capacity (f$_v$) [m^3/s]	0.00024833		
Suction pressure (p_s) [bar]	5		
Discharge pressure (p_d) [bar]	5.5		
Theoretical power [kW]	0.01241667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.04138889		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	1010
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P05	**Operating**	1
NAME	M02 feed	**Installed spare**	1
Service	T-butanol make-up		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	T-butaanol		
Temperature (T) [ºC]	25		
Density (r) [kg/m^3]	800		
Viscosity (h) [$N \cdot s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	3.55E-09		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	5.5		
Theoretical power [kW]	1.5997E-06		
Pump efficiency [-]	0.3		
Power at shaft [kW]	5.33E-06		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	784.8
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P06	**Operating**	1
NAME	C01 feed	**Installed spare**	1
Service	Solvent recycle beginning		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	T-butanol/water/debris mixture		
Temperature (T) [ºC]	70		
Density (r) [kg/m^3]	947		
Viscosity (h) [$N \cdot s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	0.00035278		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.01763889		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.0587963		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	929
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P07	**Operating**	1
NAME	M03 effluent	**Installed spare**	1
Service	Centrifuge feed		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	T-butanol/Water mixture		
Temperature (T) [ºC]	70		
Density (r) [kg/m^3]	981		
Viscosity (h) [$N^{\cdot} s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	0.00010833		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.00541667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.01805556		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	962.4
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P08	**Operating**	1
NAME	S06 feed	**Installed spare**	1
Service	Cyclone feed		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/PHB mixture		
Temperature (T) [ºC]	70		
Density (r) [kg/m^3]	997		
Viscosity (h) [$N \cdot s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	7.53333E-05		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.003766667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.012555556		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	978.1
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P09	**Operating**	1
NAME	C01 top	**Installed spare**	1
Service	Water effluent		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/Debris mixture		
Temperature (T) [ºC]	80		
Density (r) [kg/m^3]	1010		
Viscosity (h) [$N^{\cdot} s/m_2$]	2.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	0.00035833		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.01791667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.05972222		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	990.8
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P10	**Operating**	1
NAME	S07 water	**Installed spare**	1
Service	Water recycle		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water		
Temperature (T) [ºC]	80		
Density (r) [kg/m^3]	997		
Viscosity (h) [$N^{\cdot} s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	0.00034667		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	2		
Theoretical power [kW]	0.03466667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.11555556		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	978.1
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P11	**Operating**	1
NAME	S07 debris	**Installed spare**	1
Service	Debris removal		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/debris mixture		
Temperature (T) [ºC]	80		
Density (r) [kg/m^3]	1010		
Viscosity (h) [$N \cdot s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f_v) [m^3/s]	0.00011833		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.00591667		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.01972222		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v /p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	990.8
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

EQUIPMENT NUMBER	P12	**Operating**	1
NAME	M02 feed	**Installed spare**	1
Service	Solvent recycle		
Type	Centrifugal		
Number	2		
Operating Conditions & Physical Data			
Pumped liquid	Water/butanol mixture		
Temperature (T) [ºC]	70		
Density (r) [kg/m^3]	985		
Viscosity (h) [$N \cdot s/m_2$]	1.00E-03		
Vapour pressure (p_v) [bar]		**at Temperature [ºC]**	
Power			
Capacity (f$_v$) [m^3/s]	0.000305		
Suction pressure (p_s) [bar]	1		
Discharge pressure (p_d) [bar]	1.5		
Theoretical power [kW]	0.01525		
Pump efficiency [-]	0.3		
Power at shaft [kW]	0.05083333		
Construction details			
RPM	3000	**Nominal diameter**	
Drive	Electrical	**Suction Nozzle**	
Type electrical motor		**Discharge Nozzle**	
Tension	380	**Cooled Bearings**	
Rotational direction	Clock-wise	**Cooled Stuffing box**	
Foundation plate	Combined	**Smothering Gland**	
Flexible coupling	Yes	**If yes**	
Pressure Gauge Suction	No	**-Seal Liquid**	
Pressure Gauge Discharge	Yes	**-Splash Rings**	
Min. Overpressure Above p_v/p_m [bar]	0.1	**-Packing Type**	
		-Mechanical Seal	
		-N.P.S.H. [m]	966.3
Construction materials			
Pump house	MS	**Wear Rings**	
Pump rotor	HT Steel	**Shaft Box**	
Shaft	HT Steel		
Special provisions	None		
Operating pressure [bar]	5	**Test Pressure [bar]**	

MIXER UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER	M02
NAME	Cell - solvent mixer

General Data

Service		Cell resuspension
Type		Continually stirred mixer
Position		Vertical
Volume	**[m3]**	1.55
Diameter	**[m]**	1.00
Length	**[m]**	1.97
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	1.08
liquid height holdup	**[m]**	1.38
Maximum load	**[kg]**	1345.05
holdup time	**[sec]**	900

Process Conditions

Stream Details		**Solvent Recycle**	**t-butanol makeup**	**Cells**	**Liquid out**
Temp.	**[^{o}C]**	75.8	25	40	70.75
Pressure	**[bara]**	1	1	1	1
Density	**[kg/m^{3}]**	851	781	979	869
Mass Flow	**[kg/s]**	0.413	4.17E-11	0.112	0.525
Composition		**wt%**	**wt%**	**wt%**	**wt%**
water		60.4	0	57.5	59.8
t-butanol		39.5	100	0.0	31.0
PHB		0.09	0	31.9	6.9
Debris		trace	0	10.6	2.3

Remarks:
material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

MIXER UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER	M03
NAME	raw PHB - solvent mixer

General Data

Service		PHB resuspension
Type		Continually stirred mixer
Position		Vertical
Volume	**[m3]**	0.88
Diameter	**[m]**	1.00
Length	**[m]**	1.12
thickness wall	**[mm]**	5.0
liquid volume holdup	**[m3]**	0.62
liquid height holdup	**[m]**	0.79
Maximum load	**[kg]**	760
holdup time	**[sec]**	900

Process Conditions

Stream Details		**solvent - cooled**	**raw PHB**	**PHB suspension**	
Temp.	**[°C]**	70	77.1	71.7	
Pressure	**[bara]**	1	1	1	
Density	**[kg/m^3]**	774	861	786	
Mass Flow	**[kg/s]**	0.201	7.03E-02	0.271	
Composition		**wt%**	**wt%**	**wt%**	
water		18.5	31.2	21.8	
t-butanol		81.5	16.2	64.6	
PHB		trace	50.9	13.2	
Debris		trace	1.7	0.4	

Remarks:
material of construcion: SS 18/8

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	28/07/2004

DISTILLATION COLUMN - SPECIFICATION SHEET

EQUIPMENT NUMBER	C01		
NAME	T-butanol/Water Splitter		

General Data

Service	distillation		
Column Type	random packed		
Tray Type	-		
Tray Number (1)			
- Theoretical	9		
- Actual	9		
- Feed (actual)	1		
Tray Distance (HETP) [m]	0.500	**Tray material**	Nutter ring #1
Column Diameter [m]	0.310	**Column material**	SS 18/8
Column Height [m]	5	**#Rings per m^3**	67100
Heating	none		

Process Conditions

Stream Details	**Feed**		**Top**		**Bottom**		**Absorbent**			
Temp. [^oC]	77.1 ^oC		80.8 ^oC		99.8 ^oC		300.0 ^oC			
Pressure [bara]	1		1		1.015		1.015			
Density [kg/m^3]	861		1.62		918		0.386			
Mass Flow [kg/s]	0.454		0.184		0.343		0.0736			
Composition	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**	**mol%**	**wt%**
water	88.8	64.2	47.2	17.9	100	96.8	100	100		
t-butanol	11.2	33.3	52.7	82.1	0.00	0.00	0.00	0.00		
PHB		0.2		0.0		0.1		0.00		
Debris		2.3		0.0		3.1		0.00		

Column Internals *(4)*

Packing	
Type	Nutter Ring #1
Material	SS 18/8
Volume [m^3]	1.36
Length [m]	-
Width [m]	-
Height [m]	-
Number of rings	91161

Remarks:

(1) Tray numbering from top to bottom.
(2) SS = Stainless Steel

Designers	D. Lloyd	Project ID-Number	CPD3310
		Date	18/07/2004

EQUIPMENT NUMBER	E01	In Series	1
NAME	Air feed	In Parallel	None
General Data			
Service	Heat exchanger		
Type	Fixed Tube Sheets		
Position	Vertical		
Capacity [kW]	127381.50		
Heat exchange area [m^2]	0.74		
Overall heat transfer coefficient [W/m^2.ºC]	0.85		
Log. Mean Temperature Diff. (LMTD) [ºC]	849.16		
Passes tube side	1		
Passes shell side	1		
Correction factor LMTD (min. 0.75)	1		
Corrected LMTD [ºC]	849.16		

Process Conditions

	Shell side	**Tube side**
Medium	Air	Gasification effluent
Mass stream	2700	5743.32
Mass stream to		
-Evaporate	2700	-
Average specific heat [kJ/kg.ºC]	1	1.13
Heat of evap./condensation [kJ/kg]	210	231.22
Temperature IN [ºC]	262.76	1537.28
Temperature OUT [ºC]	900	1366.23
Pressure [bar]	5	5
Material	AISI 321	AISI 321

EQUIPMENT NUMBER	E02	In Series	1
NAME	R01 Steam supply	In Parallel	None
General Data			
Service	Heat exchanger		
Type	Fixed Tube Sheets		
Position	Vertical		
Capacity [kW]	1242.96		
Heat exchange area [m^2]	1.38		
Overall heat transfer coefficient [W/m^2.ºC]	0.85		
Log. Mean Temperature Diff. (LMTD) [ºC]	1057.28		
Passes tube side	1		
Passes shell side	1		
Correction factor LMTD (min. 0.75)	1		
Corrected LMTD [ºC]	1057.28		
Process Conditions			
	Shell side	**Tube side**	
Medium	Steam	Gasification effluent	
Mass stream	1499.99	5743.32	
Mass stream to			
-Evaporate	1499.99	-	
Average specific heat [kJ/kg.ºC]	2	1.13	
Heat of evap./condensation [kJ/kg]	2260	231.22	
Temperature IN [ºC]	37.84	1366.23	
Temperature OUT [ºC]	360	950.96	
Pressure [bar]	1	5	
Material	AISI 321	AISI 321	

EQUIPMENT NUMBER	E03	In Series	1
NAME	C01 steam feed	In Parallel	None
General Data			
Service	Heat exchanger		
Type	Fixed Tube Sheets		
Position	Vertical		
Capacity [kW]	193.27		
Heat exchange area [m^2]	0.28		
Overall heat transfer coefficient [W/m^2.ºC]	850		
Log. Mean Temperature Diff. (LMTD) [ºC]	802.06		
Passes tube side	1		
Passes shell side	1		
Correction factor LMTD (min. 0.75)	1		
Corrected LMTD [ºC]	802.06		

Process Conditions

	Shell side	**Tube side**
Medium	Steam	Gasification effluent
Mass stream	250	5743.32
Mass stream to		
-Evaporate	250	-
Average specific heat [kJ/kg.ºC]	2	1.13
Heat of evap./condensation [kJ/kg]	2260	231.22
Temperature IN [ºC]	70	950.96
Temperature OUT [ºC]	300	883.55
Pressure [bar]	1.016	5
Material	AISI 321	AISI 321

EQUIPMENT NUMBER	E04	In Series 1
NAME	M03-cooler	In Parallel None
General Data		
Service	Cooler	
Type	Fixed Tube Sheets	
Position	Vertical	
Capacity [kW]	9.08	
Heat exchange area [m^2]	0.3	
Overall heat transfer coefficient [$W/m^2.{}^{o}C$]	850	
Log. Mean Temperature Diff. (LMTD) [ºC]	35.93	
Passes tube side	1	
Passes shell side	1	
Correction factor LMTD (min. 0.75)	1	
Corrected LMTD [ºC]	35.93	
Process Conditions		
	Shell side	**Tube side**
Medium	Water	Water / Butanol
Mass stream [kg/h]	150	272.506
Mass stream to [kg/h]		
-Evaporate		242.257834
Average specific heat [kJ/kg.ºC]	4.18	4.18
Heat of evap./condensation [kJ/kg]	2260	2260
Temperature IN [ºC]	20	99
Temperature OUT [ºC]	74	70
Pressure [bar]	1	1
Material	CS	CS

EQUIPMENT NUMBER	E05	In Series	1
NAME	S07 feed cooler	In Parallel	None
General Data			
Service	Cooler		
Type	Fixed Tube Sheets		
Position	Vertical		
Capacity [kW]	-44.49		
Heat exchange area [m^2]	1.49		
Overall heat transfer coefficient [W/m^2.ºC]	850		
Log. Mean Temperature Diff. (LMTD) [ºC]	23.36		
Passes tube side	1		
Passes shell side	1		
Correction factor LMTD (min. 0.75)	1		
Corrected LMTD [ºC]	23.36		
Process Conditions			
	Shell side	**Tube side**	
Medium	Water	Water	
Mass stream	350	1211.7	
Mass stream to			
-Condense			
Average specific heat [kJ/kg.ºC]	4.18	4.18	
Heat of evap./condensation [kJ/kg]	2260	2260	
Temperature IN [ºC]	20	100	
Temperature OUT [ºC]	94	70	
Pressure [bar]	1	1	
Material	CS	CS	

PRODUCT UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		X01
NAME		SCREW 1
General Data		
Service		FEEDING SCREW 2
Type		SCREW
Barrel length	**[m]**	2.5
Screw length	**[m]**	2.5
Diameter	**[mm]**	630
Power rating	**[kW]**	5.5
Speed	**[m/s]**	0.3
Pressure	**[bar]**	5.00E+00

Process Conditions

Stream Details		**Feed**
Temp.	**[^{o}C]**	25
Density	**[kg/m^3]**	750
Mass Flow	**[KG/H]**	1550.000

Remarks:

AISI 304

PRODUCT UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		X02
NAME		SCREW 2
General Data		
Service		FEEDING GASIFIER
Type		SCREW
Barrel length	**[m]**	2.5
Screw length	**[m]**	2.5
Diameter	**[mm]**	630
Power rating	**[kW]**	22
Speed	**[m/s]**	3
Pressure	**[bar]**	5.00E+00

Process Conditions

Stream Details		**Feed**
Temp.	**[^{o}C]**	25
Density	**[kg/m^3]**	750
Mass Flow	**[KG/H]**	1550.000

Remarks:

AISI 321, As it will end up in the gasifier

PRODUCT UNIT - SPECIFICATION SHEET

EQUIPMENT NUMBER		X04
NAME		PHB extrusion
General Data		
Service		Product granulation
Type		Vented extruder
Barrel length	**[m]**	1.52
Screw length	**[m]**	1.52
L/D ratio	**[-]**	24:1
Power rating	**[kW]**	37.3
Temperature Control		liquid cooling system

Process Conditions

Stream Details		**Feed**	
Temp.	**[^oC]**	170	
Density	**[kg/m^3]**	1250	
Mass Flow	**[kg/s]**	0.037	
Composition		**mol%**	**wt%**
PHB			96.8
Debris			3.2

Remarks:

Designers	M.J ter Meulen	Project ID-Number Date

Appendix 6:
Equipment summeries

Appendix 6-1 Summary Columns, Reactors and Vessel

EQUIPMENT NR NAME	C01 T-Butanol/water	R01 Gasifier	R02 Growth reactor	R03 PHB product	R04 PHB product	R05 PHB product	V01 Wood Hop
Pressure [bara]	1	5	5	5	5	5	5
Temp. [ºC]	80.8/99.8	1300/1534	20-40	40	40	40	40
Volume [m^3]	0.38	12	8				1
Diameter [m]	0.31	1.2-1.5	1.5	1.7	1.7	1.7	0.75
L or H [m]	5	8	3	3.4	3.4	3.4	2.25
Internals			Membranes	Membranes	Membranes	Membranes	
Random Packing							
Type	Nutter Ring#1						
Catalyst							
Type		RiverSand					
Shape		Random					
Number							
Serie	1	1	1	1	1	1	
Paralel							
Special Materials of Construction		SS 321	Heat Jacket Sparger	Heat Jacket Sparger	Heat Jacket Sparger	Heat Jacket Sparger	
Other							

EQUIPMENT NR NAME	V02 Pressurised Ho	V03 Gas/liquid se	V04 Recycle water	V05 Nutrient solu	V06 Solvent buffe	V07 Hydrogen storage
Pressure [bara]	5	5	5	1	1	50
Temp. [ºC]	25	40	40	40	70	40
Volume [m^3]	5	1	5	5	5	5
Diameter [m]	1.25	0.75	1.25	1.25	1.25	1.25
L or H [m]	4.07	2.25	4.07	4.07	4.07	4.07
Internals						
Random Packing						
Type						
Catalyst						
Type						
Shape						
Number						
Serie						
Paralel						
Special Materials of Construction						
Other						

Appendix 6-2

Summary Heat Exchangers

EQUIPMENT NR:	E01	E02	E03	E04	E05
NAME:	Air feed	R01 Steam supply	C01 steam feed	M03-cooler	S07 feed cooler
Substance					
-Tubes	Gasification effluent	Gasification effluent	Gasification effluent	Water / Butanol	Water
-Shell	Air	Steam	Steam	Water	Water
Duty [kW]	127381.501	1242.96	193.27	9.08	-44.49
Heat exchange area [m2]	0.74	1.38	0.28	0.3	1.49
Number					
-Series	1	1	1	1	1
-Parallel	None	None	None	None	None
Pressure [bar]					
-Tubes	5	5	5	1	1
-Shell	5	1	1.016	1	1
Temperature In [ºC]					
-Tubes	1537.28	1366.23	950.96	99	100
-Shell	262.76	37.84	70	20	20
Temperature Out [ºC]					
-Tubes	1366.23	950.96	883.55	70	70
-Shell	900	360	300	74	94
Special Materials of Construction	AISI 321	AISI 321	AISI 321	CS	CS
Other					

EQUIPMENT NR	P01	P02	P03	P04	P05	P06	P07	P08	P09
NAME	Water feed	Water feed	R02 feed	R05 effluent	M02 feed	C01 feed	M03 effluer	S06 feed	C01 top
Type	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal
Number	2	2	2	2	2	2	2	2	2
Medium									
Transferred	Water	Water	Water/Nutr	Water and b	T-butaanol	T-butanol/v	T-butanol/V	Water/PHB mixtu	Water/Debr
Capacity									
[kg/s]	0.0557323	0.0557323	0.234295	0.2557833	2.84387E-06	0.334081	0.106275	0.075107333	0.361917
[m3/s]	0.0000559	0.0000559	0.000235	0.0002483	3.55483E-09	0.000353	0.000108	7.53333E-05	0.000358
Density [kg/m3]	997	997	997	1030	800	947	981	997	1010
Pressure [bara]	1	1	1	5	1	1	1	1	1
Suct./Disch.	5	5	5	5.5	5.5	1.5	1.5	1.5	1.5
Temperature	25	25	25	40	40	40	40	40	40
In/Out [ºC]	25	25	25	40	40	40	40	40	40
Power [kW]									
- Theor	0.02236	0.02236	0.094	0.0124167	1.59968E-06	0.017639	0.005417	0.003766667	0.017917
- Actual	0.0745333	0.0745333	0.313333	0.0413889	5.33225E-06	0.058796	0.018056	0.012555556	0.059722
Number									
- Theor									
- Actual									
Special Materials of Construction									
Other									

EQUIPMENT NR	P10	P11	P12	P13	K01	K02	K03	K04	K05
NAME	S07 water	S07 debris	M02 feed	S03 Permea	R01-Methane fee	R01 feed	R01-steam	R02 feed	S06 feed
Type	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Centrifugal	Two stage	Two stage	Two stage turboc	Centrifugal
Number	2	2	2	2	2	1	1	1	2
Medium									
Transferred	Water	Water/debr	Water/buta	Water/cells	Methane	Air	Steam	Syn-gas	Water/t-but
Capacity									
[kg/s]	0.3456267	0.1195167	0.300425	0.1851667	0.0407	13.0662	3.51	0.00605	1453.5
[m3/s]	0.0003467	0.0001183	0.000305	0.0001833	0.074	5	10	5.5	1.5
Density [kg/m3]	997	1010	985	1010	0.55	2.61324	0.351	0.0011	969
Pressure [bara]	1	1	1	1	1	182.59	323.27	15.5	5.194167
Suct./Disch.	2	1.5	1.5	1.5	5	0.72	0.72	0.72	0.72
Temperature	80	80	70	40	25	25	360	24.7	99
In/Out [ºC]	80	80	70	40	212.5	262.9	722	73.8	146.3
Power [kW]									
- Theor	0.0346667	0.0059167	0.01525	0.0091667	29.6	253.5972	448.9861	21.52777778	7.21412
- Actual	0.1155556	0.0197222	0.050833	0.0305556	98.66666667	3000	3000	3000	3000
Number									
- Theor									
- Actual									
Special Materials of Construction									
Other									

Appendix 6-4 Summary Mixers ans Separators

EQUIPMENT NR:	S01	S02	S03	S04	S05
NAME:	Syngas cleanup	Syngas Filter	Broth Concentr	Raw PHB recovery	Pure PHB recovery
Substances separated	Syngas Ash	Syngas Ash	Cells Water	PHB Water	PHB Water
Pressure [bar]	5	5	5	1	1
Temperature [ºC]	884	884	40	77	71.7
Number					
-Series	1	2	1	1	1
-Parallel					
Volume [m^3]	0.43	n.a.	0.001	-	-
Capacity [kg/s]	1.6	1.6	0.112	0.525	0.271
Capacity [m^3/s]	1.39	1.39	1.10E-04	5.50E-04	3.40E-04
Special Materials of Construction		Ceramic filter	Polyester membrane		
Other					

EQUIPMENT NR:	S06	S07	M02	M03
NAME:	Pure PHB recove	Debris Remova	Cell solvet mix	Raw PHB solvent Mixer
Substances separated	PHB Water	Debris Water	Cell + t-butano Water	PHB + t-butanol Water
Pressure [bar]	1	1	1	1
Temperature [ºC]	83-85	99.8	25-75	70-77
Number				
-Series	1	1	1	1
-Parallel				
Volume [m^3]	-	-	1.55	0.88
Capacity [kg/s]	0.237	0.343	0.525	0.271
Capacity [m^3/s]	0.135	3.70E-04	6.00E-04	3.40E-04
Special Materials of Construction				
Other				

Summary of utilities

Equipment		Utilities													
		Heating					Cooling				Power				
			Concumption (t/h)					Consumption (t/h)				Consumption (t/h, kWh/h)			
			Steam									Steam (t/h)			
Nr	Name	Load kW	LP	MP	HP	Hot oil	Load	Cooling water	Air	Refrig.	Actual Load	HP	MP	Electr. kWh/h	Remarks
E01	Air feed														
E02	R01 Steam supply														
E03	C01 Steam feed														
E04	M03-Cooler						9.08	0.15							
E05	S07 feed cooler						-44.49	0.35							
E06	Syngas cooler														
P01	Water feed										0.075			0.075	
P02	Water feed fermentation										0.075			0.075	
P03	Nutrient mixture inflow pump										0.31			0.31	
P04	R05 effluent										0.041			0.041	
P05	M02 feed										5.3E-06			5.3E-06	
P06	C01 feed										0.059			0.059	
P07	M03 Effluent										0.018			0.018	
P08	S06 feed										0.012			0.012	
P09	C01 top										0.06			0.06	
P10	S07 water										0.12			0.12	
P11	S07 debris										0.02			0.02	
P12	M02 feed										0.031			0.031	
P13	S03 Permeate														
											148.78			148.78	
K01	R01 methane feed										304.84			304.84	
K02	R01 feed										255			255	
K03	R01-steam										363.44			363.44	
K04	R02 feed										17.31			17.31	
K05	S06 feed														
S04	Raw PHB Recovery										0.745			0.745	
S05	Pure PHB Recovery (wet)										0.745			0.745	
S07	Debris removal										0.745			0.745	

Project ID Number: CPD3310
Completion Date: 29-7-2004

Appendix 7:
Economy

UTILITY COSTS, EXCL. VAT (1) APPENDIX 7-1

Utility	Units (2)		LHV	Unit Costs, E/unit			
	Quant.	Energy	En. per Quant.	Quant.		Energy	
				Min.	Max.	Min.	Max.
NG	Nm3	MJ	31.65	0.15	0.30	0.00474	0.009478673
	kg	MJ	37.68	0.18	0.36	0.00474	0.009478673
	ton	MJ	37678.57	178.57	357.14	0.00474	0.009478673
HFO	ton	MJ	41.45	127.06	136.13	3.06534	3.284295895
Coal	ton	MJ	26400.00	49.92	70.20	0.00189	0.002659091
Steam LP/HP	ton			20.00	22.00		
Electricity	(4)	kWh				0.06	0.12
Cooling Water	m3			0.05	0.10		
BFW/Process W	m3			0.50	1.13		
Presur. Air	Nm3			0.02			

Remarks

1. Ref. "Cost Data, WEBCI / DACE", 18th Edition November 1995
2. 1 ton = 1000 kg
3. Density : 0.84 kg/Nm3 , MW : 18.60
4. For quantities > 10^6 kWh/a
5. Air press 7 Bara
6. All prices except BFW and Press.Air from DACE 2003
7. Rate of Exchange Euro's/guilders 2.20371

HEAT EXCHANGERS

NUMBER	POWER [kW]	TYPE	MASS FLOW [KG/H]	MASSFLOW [T/Y]	CW [T/Y]	BFW [T/Y]	STOOM [T/Y]	ELECT [KWH/Y]	AIR [NM3/Y]	CH4 [NM3/Y]
E01		AIR	2700	21600					18000000	
E02		STEAM	1500	12000			12000			
E03		STEAM	250	2000			2000			
E04		WATER	150	1200	1200					
E05		WATER	350	2800	2800					
E06		AIR		0						
COMPRESSORS										
P01	0.07							506.83		
P02	0.07							506.83		
P03	0.31							2130.67		
P04	0.04							281.44		
P05	0.00							0.04		
P06	0.06							399.81		
P07	0.02							122.78		
P08	0.01							85.38		
P09	0.06							406.11		
P10	0.12							785.78		
P11	0.02							134.11		
P12	0.05							345.67		
P13	0.03							207.78		
K01	148.78							1011688.89		
K02	304.84							2072939.09		
K03	255.00							1734000.00		
K04	363.44							2471363.67		
K05	17.31							117734.44		
PROCESS WATER										
STREAM	42		216			1728				
STREAM	54		828			6624				
PROCESS METHANE										
		R01	396							38016
OPERATION	96	H/Y	[Nm3/h]							
PROCES AIR										
		R01	2700							
		R02-R05	8892						59280000	
MEMBRANES										
R02-R05			SURFACE [M2]	38000						
					4000	**8352**	**14000**	**7413639.31**	**77280000**	**38016**
					CW [T/Y]	**BFW [T/Y]**	**STOOM [T/Y]**	**ELECT [KWH/Y]**	**AIR [NM3/Y]**	**CH4 [NM3/Y]**

Remark, it was found that the use of methane is much less than assumed, see below. As this has a significant (positive) effect on the economics while these had already been determined, this value could not be entered anymore. So this is a slight overdesign…

PRODUCTS COSTS PER UNIT

PRODUCT	**UNIT**	**AMOUNT /tonne**	**PRICE /EUR/t**	**TOTAL PRICE/EUR**
PHB	ton	1008	10000	10080000
total		*1008*	*10000*	*10080000*
BYPRODUCT				
ASH		56	0	0
The ash is sold to the cement industry for very low prices to make sure it will be accepted				
total		*56*	*0*	*0*
WASTE			**COST /EUR**	
WATER STREAM 95	TON	1440	0.1	144
WATER STREAM 52	TON	4896	0.1	489.6
waste water discharge costs EUR5/tonne…				
total		*6336*	*0.2*	*633.6*
TOTAL				10079366.4

RAW MATERIALS COST PER UNIT

RAW MAT	**UNIT**	**AMOUNT /tonne/Y**	**PRICE /EUR/t**	**TOTAL PRICE/EUR**
WOOD	ton	12400	13	161200
TERT-BUTAI	TON	5	1250	6250
NUTRIENTS	ton	134	245	32800
SAND	ton	12	20	240
total				*200490*
TOTAL				200490

CAPITAL COSTS

REACORS & COLUMNS										
NAME	**EQUIPMENT**	**TYPE, FIGURE QUANT**	**DIAM /M CURVE**	**H /M COSTS /EUR**	**M OF C FAC**	**PRESS /BAR FAC**	**COSTS EQUIP /EUR**	**COSTS INTERN /EUR**		**COSTS TOTAL /EUR**
R01	column	Vert	D=1.5	15	AISI 321	5				
		wall thick=12mm		119000			119000	1060	plate	120060
R02	column	vert		5		5				
		wall thck=8mm		52000	SS 18/8		52000			52000
			D=1.5							
R03	column	vert		5		5				
		wall thck=8mm		52000	SS 18/8		52000			52000
			D=1.5							
R04	column	vert		5		5				
		wall thck=8mm		52000	SS 18/8		52000			52000
			D=1.5							
R05	column	vert	L=5	5		5				
		wall thck=8mm		52000	SS 18/8		52000			52000
			D=1.5							
C01				5						
				28000	SS 18/8		28005	5712	pall ring 16mm	33717
			D=0.5							
	REMARKS (1) For R01 AISI SS321 was needed. It was chosen to take the higher price of AISI 316 and a bigger column to compensate for the strange form of the reactor, which clearly is not standard. (2) Furthermore, another reason to select a slightly bigger column would be to compensate for the exclusion of transport etc in the costs									
subtotal										361777
BTW									19%	68737.63
TOTAL		**REACTORS**								**792291.63**

CAPITAL COSTS

HEAT EXCHANGERS									
NAME	**M OF C SH/TUBES**	**CURVE**	**SURFACE /M2**	**COSTS /EUR**	**TYPE**	**FACTOR**	**PRESS /BAR**	**FACTOR**	**COSTS /EUR**
E01	AISI 321		2				5		19000
E02	AISI 321		2				5		19000
E03	AISI 321		2				5		19000
E04	CS		2				1		8000
E05	CS		2				1		8000
E06	CS		2				1		8000
subtotaal									81000
BTW								19%	15390
TOTAL									**96390**

CAPITAL COSTS

COMPRESSORS & EXPANDERS					
NAME	**CAPACITEIT** **M3/s** m3/h	**P** **kW**	**TYPE** **RPM** **0**	**PRICE PUMP** **/EUR**	**PRICE E-MOTOR** **/EUR**
K01	0.11	150	SSSC	70000	25000
	396		3000		
K02	0.64	254	SSSC	85000	30000
	2304		1500		
K03	1.2	450	SSSC	183000	64000
	4320		3000		
K04	0.228	22	SSSC	39000	8000
	820.8		1500		
K05	0.1	7	SSSC	26000	4000
	360		3000		
P01		0.07	SSCP	3300	140
	0.2		3000		
P02		0.07	SSCP	3300	140
	0.2		3000		
P03		0.31	SSCP	3300	140
	0.85		3000		
P04		0.04	SSCP	3300	140
	0.9		3000		
P05		0	SSCP	3300	140
	0		3000		
P06		0.06	SSCP	3300	140
	1.27		3000		
P07		0.02	SSCP	3300	140
	0.39		3000		
P08		0.01	SSCP	3300	140
	0.27		3000		
P09		0.06	SSCP	3300	140
	1.29		3000		
P10		0.12	SSCP	3300	140
	1.25		3000		
P11		0.02	SSCP	3300	140
	0.43		3000		
P12		0.05	SSCP	3300	140
	1.1		3000		
P13		0.03	SSCP	3300	140
	0.66		3000		
SUBTOT	COMP			403000	131000
	PUMP			85800	3640
	BTW		19%	92872	25581.6
TOTAL COMPRESSORS & EXPANDERS					**741893.6**

Pumps were counted double (incl. Spare)

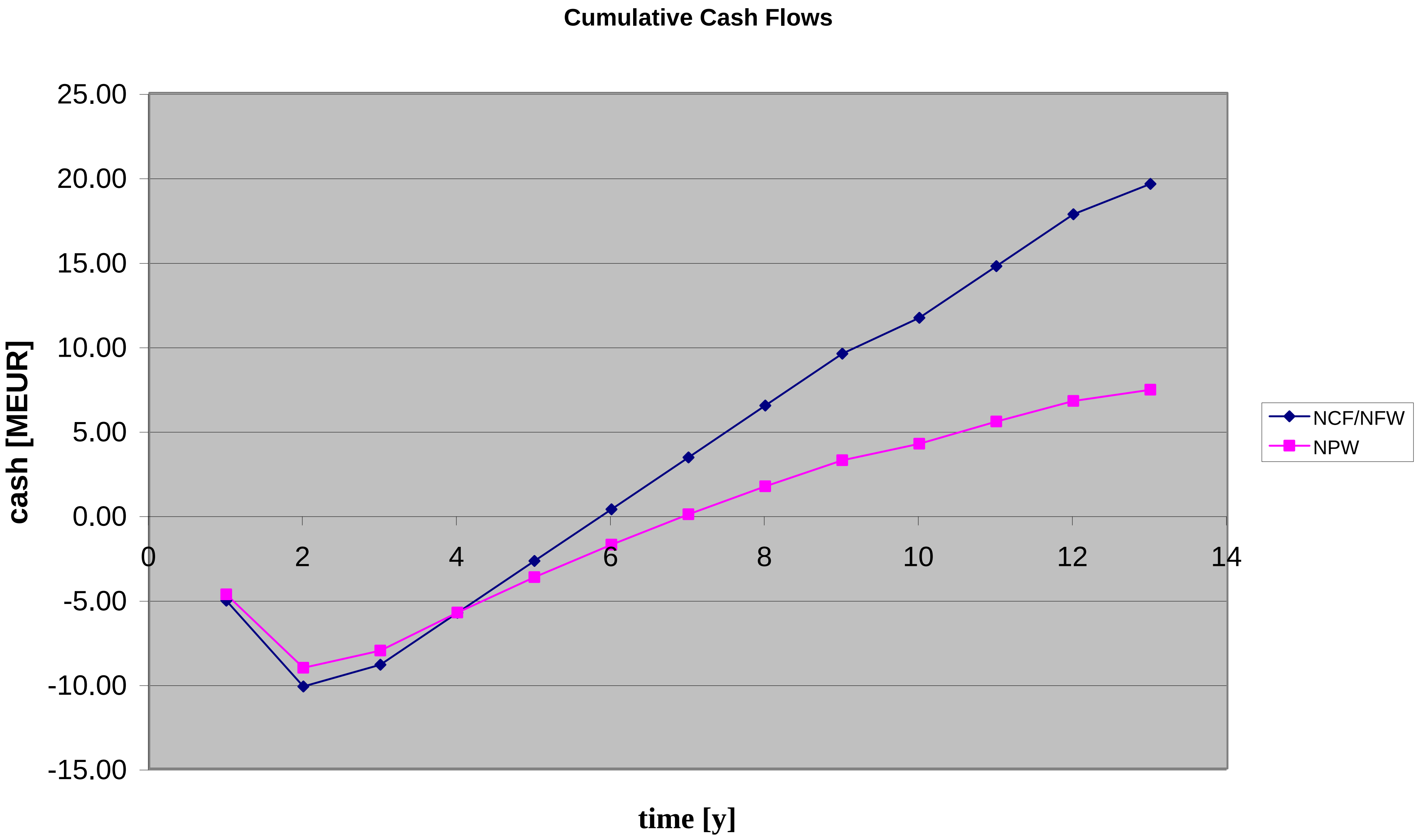
SSSC	SINGLE-STAGE SCREW COMPRESSOR
SSCP	SINGLE-STAGE CENTRIFUGAL PUMP

CAPITAL COSTS

MIXERS&SEPARATORS										
NAME	**EQUIPM**	**TYPE, FIGURE QUANT**	**DIAM /M CURVE**	**H /M COSTS /EUR**	**M OF C FAC**	**PRESS /BAR**	**COSTS EQUIP /EUR**	**COSTS INTERN /EUR**		**COSTS TOTAL /EUR**
V03	VESSEL				AISI 304	5				8500
S01	CYCLONE			typical price HE cyclone	AISI 321 more expenive steel		12000			18000
S02	CERAMIC FILTER		see Appendix price for two filters							129000
S03	VESSEL				POLYPROPYL	5	4000 price from CS	1500	membrane	5500
M01	VESSEL	V [M3] 1			STEEL HII					11000
M02	VESSEL	V [M3] 1.5			AISI 304	1				23000
M03	VESSEL	V [M3] 1			AISI 304	1				18000
S04	(DISK) CENTRIFU	DIAMETER [M] 0.5			AISI 304	1				33000
S05	(DISK) CENTRIFU	DIAMETER [M] 0.5			AISI 304	1				33000
S06	CYCLONE ARRAY		# 3				10000			30000
S07	(DISK) CENTRIFU	DIAMETER [M] 0.5			AISI 304	1				33000
	subtotal									342000
	BTW								19%	64980
TOTAL		**MIXERS&SEPARATORS**								**406980**

CAPITAL COSTS

MISCELLANEOUS											
NAME	**EQUIPMENT**	**TYPE, FIGURE QUANT**	**CARACTERISTIC [UNIT]**			**M OF C FAC**	**PRESS /BAR**	**POWER [kW]**	**COSTS INTERN /EUR**		**COSTS TOTAL /EUR**
A01	HAMMER MILL		SEE APPENDIX								70000
A02	HOMOGENIZE	PUMP	FLOW [M3/h]					6.5			4040
				2.2							
A03	HOMOGENIZE	PUMP	FLOW [M3/h]					6.5			4040
				2.2							
V01	HOPPER		V [M3]			POLYESTER	1				
				100							17000
V02	HOPPER		V [M3]			AISI 304	5				
				10							26000
V04	VESSEL		V [M3]			PVC	1				5000
				3							
V05	VESSEL		V [M3]			AISI 304	1				8000
				3							
X01	SCREWS		L [M]		D [MM]						
				2.5	630			5.5	*8000*	2200	2200
				2.5	630			22	*8000*	6520	6520
X02	CONVEYOR		WIDTH [M]		LENGTH [M]					PRICE/M	25625
	BELT			1	25					1025	
X03	IDEM										25625
X04	IDEM										25625
			L [M]		D [MM]						
	EXTRUDER			*2.5*	*315*			*37.3*	*5520*	*11780*	*17300*
	HOPPER		L [M]		D [MM]						
				5.9	*2.4*	*GRP*			*2000*	*7000*	*9000*
	the hopper costs 7000, 2000 extra is added to strengthen the construction as the max. load is 500kg/m3										
Numbers in Italics are not counted in the total sum, as they were calculated AFTER the economical evaluation!!!											
TOTAL											219675
BTW										19%	41738.25
TOTAL											**261413.25**


Cumulative Cash Flows
cash [MEUR]
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-10.00
-15.00
0
2
4
6
8
10
12
14
time [y]
NCF/NFW
NPW

step		price wood/t	wood feed	price non-wood	non wood feed	price utilities	capital invest	people	tax	BTW	interest	cost price PHB	sell price PHB	amount PHB	Gross Income	ROR	Pay-Back Time	NCF	NFW	NPW	NCFRR
starting values		13	12400	505	151	1224000	12000000	1125000	45	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
price wood	10	14.3	12400	505	151	1224000	12000000	1125000	45	19	8	6.973	10	1008	10080	32	3	4064	19.42	7.31	20.4
	-10	11.7	12400	505	151	1224000	12000000	1125000	45	19	8	6.936	10	1008	10080	32	3	4102	19.79	7.52	20.6
wood feed	10	13	13640	505	151	1224000	12000000	1125000	45	19	8	7.028	10	1000	10002	31	3	3987	18.64	6.86	19.6
	-10	13	11160	505	151	1224000	12000000	1125000	45	19	8	6.86	10	1019	10192	33	3	4214	20.91	8.16	21.6
price non-wood	10	13	12400	555.5	151	1224000	12000000	1125000	45	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
	-10	13	12400	454.5	151	1224000	12000000	1125000	45	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
non wood feed	10	13	12400	505	166.1	1224000	12000000	1125000	45	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
	-10	13	12400	505	135.9	1224000	12000000	1125000	45	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
price utilities	10	13	12400	505	151	1346400	12000000	1125000	45	19	8	7.113	10	1008	10080	30	3	3923	18.01	6.5	19
	-10	13	12400	505	151	1101600	12000000	1125000	45	19	8	6.816	10	1008	10080	33	3	4224	21.01	8.22	22
capital investme	10	13	12400	505	151	1224000	13200000	1125000	45	19	8	7.244	10	1008	10080	27	4	3893	15.67	4.76	15.6
	-10	13	12400	505	151	1224000	10800000	1125000	45	19	8	6.666	10	1008	10080	38	3	4273	23.53	10.07	26
people	10	13	12400	505	151	1224000	12000000	1237500	45	19	8	7.199	10	1008	10080	30	3	3837	17.14	6	18.3
	-10	13	12400	505	151	1224000	12000000	1012500	45	19	8	6.711	10	1008	10080	34	3	4328	22.06	8.83	22.5
tax	10	13	12400	505	151	1224000	12000000	1125000	49.5	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
	-10	13	12400	505	151	1224000	12000000	1125000	40.5	19	8	6.955	10	1008	10080	32	3	4083	19.6	7.41	20.5
BTW	10	13	12400	505	151	1224000	12000000	1125000	45	20.9	8	6.994	10	1008	10080	31	3	4057	19.07	7.06	19.8
	-10	13	12400	505	151	1224000	12000000	1125000	45	17.1	8	6.916	10	1008	10080	33	3	4109	20.13	7.77	21.2
interest	10	13	12400	505	151	1224000	12000000	1125000	45	19	8.8	6.955	10	1008	10080	32	3	4082	19.6	6.64	20.5
	-10	13	12400	505	151	1224000	12000000	1125000	45	19	7.2	6.955	10	1008	10080	32	3	4082	19.6	8.24	20.5
sell price PHB	10	13	12400	505	151	1224000	12000000	1125000	45	19	8	6.955	11	1008	11088	42	2	5091	29.68	13.21	29
	-10	13	12400	505	151	1224000	12000000	1125000	45	19	8	6.955	9	1008	9072	22	5	3075	9.52	1.62	11

step		price wood/t	wood feed	price non-wood	non wood feed	price utilities	capital invest	people	tax	BTW	interest	cost price PHB	sell price PHB	amount PHB	Gross Income	ROR	Pay-Back Time	NCF	NFW	NPW	NCFRR
starting values		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
price wood	10	10	0	0	0	0	0	0	0	0	0	0.26	0	0	0	0	0	-0.47	-0.92	-1.35	-0.49
	-10	-10	0	0	0	0	0	0	0	0	0	-0.27	0	0	0	0	0	0.47	0.97	1.48	0.49
wood feed	10	0	10	0	0	0	0	0	0	0	0	1.0496	0	-0.79365079	-0.773809524	-3.125	0	-2.35121	-4.89796	-7.4224	-4.39024
	-10	0	-10	0	0	0	0	0	0	0	0	-1.36592	0	1.09126984	1.111111111	3.125	0	3.20843	6.68367	10.1215	5.36585
price non-wood	10	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	-10	0	0	-10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
non wood feed	10	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	-10	0	0	0	-10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
price utilities	10	0	0	0	0	10	0	0	0	0	0	2.27	0	0	0	-6.25	0	-3.92	-8.11	-12.28	-7.32
	-10	0	0	0	0	-10	0	0	0	0	0	-2.00	0	0	0	3.125	0	3.45	7.19	10.93	7.32
capital investme	10	0	0	0	0	0	10	0	0	0	0	4.16	0	0	0	-15.63	33.33	-4.65	-20.05	-35.76	-23.90
	-10	0	0	0	0	0	-10	0	0	0	0	-4.16	0	0	0	18.75	0	4.65	20.05	35.90	26.83
people	10	0	0	0	0	0	0	10	0	0	0	3.51	0	0	0	-6.25	0	-6.02	-12.55	-19.03	-10.73
	-10	0	0	0	0	0	0	-10	0	0	0	-3.51	0	0	0	6.25	0	6.00	12.55	19.16	9.76
tax	10	0	0	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0
	-10	0	0	0	0	0	0	0	-10	0	0	0	0	0	0	0	0	0	0	0	0
BTW	10	0	0	0	0	0	0	0	0	10	0	0.56	0	0	0	-3.125	0	-0.64	-2.70	-4.72	-3.41
	-10	0	0	0	0	0	0	0	0	-10	0	-0.56	0	0	0	3.125	0	0.64	2.70	4.86	3.41
interest	10	0	0	0	0	0	0	0	0	0	10	0	0	0	0	0	0	-0.02	0	-10.39	0
	-10	0	0	0	0	0	0	0	0	0	-10	0	0	0	0	0	0	-0.02	0	11.20	0
sell price PHB	10	0	0	0	0	0	0	0	0	0	0	0	10	0	10	31.25	-33.33	24.69	51.43	78.27	41.46
	-10	0	0	0	0	0	0	0	0	0	0	0	-10	0	-10	-31.25	66.67	-24.69	-51.43	-78.14	-46.34

Appendix 8:
Visits to experts

8-1 Interview with ir. W. de Jong

ir. W. de Jong is assistant professor of the Energy Technology section, department of Mechanical engineering and maritime technology, Delft University of Technology

On the advise of prof. Moulijn a consultation with ir. W. de Jong was arranged. Ir. De Jong works at OCP, a subgroup of Mechanical Engineering. There, they have a fluidised bed for biomass gasification, this is the same as the unit that needs to be designed. Unfortunately the bed had been disassembled, so it could not be viewed, but ir. De Jong had designed, supervised and worked with it and was glad to talk about the fluidised bed.

Biomass availability and reaction kinetics were discussed. A clear picture of typical dimensions and rates for the reactor were gained. It was now possible to compare results calculated using models with realistic values provided by De Jong. He also approved our Aspen model, but stressed again that the kinetics would determine the real reactor.

In choosing the reactor type (CFB, FBR, two CFR's - Silva process, Carbo-V, Lurgi, entrained flow etc.) the advise of De Jong was also invaluable. A decision had already been taken to design a FBR, or maybe a CFB. This was because the other reactors were quite difficult to design properly or because of technical complications or capacity reasons. We were lucky to be confirmed in our choice. Indeed a 'simple' model would be enough work for a relatively small (on time scale) project like CPD.

Additionally, de Jong provided a number of articles and other literature, which proved to be very useful.

8-2 Visit to Prof. van Loosdrecht

Professor Van Loosdrecht works as a professor of bioprocess-technology at the section of environmental biotechnology at the TU-Delft. He has carried out research on the production of PHB.

This consultation was carried out at an early phase of the project. The conversation / questions were mostly of a general nature. Subjects discussed were: bacteria substrate use, genetic manipulation, downstream processing and the possibility of converting a biomass feedstock. This consultation helped the team on its way concerning process and feedstock options. Some options or possibilities could be immediately eliminated because of the expert’s advice, whilst on the other hand some general assumptions could be made without the need to find confirmation in the literature. For example the use of genetic manipulated micro-organism was not advised, since metabolic engineering often affects other metabolic routes and thus decreases productivity or cell growth. An example of the general assumption that could be made is that almost every bacteria makes PHB as a storage material.

8-3 Visit to Dr R.G.J.M. van der Lans and M. Hoeben

The visit to these two experts was the result of the search for an alternative solvent for separation of PHB from cell debris. Dr. Van der Lans has previously published on the use of t-butanol for the separation of nano-bioparticles and Mr Hoebel is engaged in a PhD on the topic of a bioparticle recovery system.

Initially the discussion focused on the nature of the impurity to be removed. Was the impurity a well formed membrane or was it other cell debris? After briefly introducing the publications which the group had used and further discussion a consensus was reached that the impurity was all the other cell debris. The question was then exactly how SDS could prevent the cell debris from sedimenting during centrifugation.

By comparing the behaviour of large biomolecules in the t-butanol/water precipitation system to the behaviour of debris in the SDS solution the similarity between the two systems could be identified. On the basis of this Dr. Van der Lans pronounced that the mechanism proposed to separate PHB from other cell debris was consistent and plausible.

8-4 Visit to dr.ir. R.G.J.M. van der Lans

Dr. Van der Lans is the assistant professor of solids separation at the department of bioseperations at the TU-Delft.

The objective of this consultation was to get more insight in the designing of membrane aeration reactors. The main problem was the choice between closed end and open-end membranes. Furthermore the balance derived at that moment didn’t give reasonable results.

Van der Lans first told us that membrane aeration reactors already exist, but that they are not common. From his description of such a reactor it was clear that a reactor can be completely filled with membranes and can still contain an agitator.

Regarding the choice between closed end and open-end membranes he advised to use open end. The reason for this was that the mass transfer in closed end membranes is severely limited by the high nitrogen concentration. He also advised to neglect the pressure drop of the syn-gas through the membranes, since pressure drop of gases through straight tubes is practically zero. The visit was essential for the derivation of the correct mass balances. Furthermore the fact that Van der Lans had seen these reactors in an industrial setting removed any the uncertainty of that such a reactor design cannot meet the requirements.

8-5 Visit to Prof. Heijnen

Heijnen works as a professor in bioprocess-technology at the section of bioprocess-technology at the TU-Delft.

This was a more specific consultation than the one with prof. Van Loosdrecht. In this case we wanted to exploit the possibilities of syn-gas fermentation. We found some literature on these fermentations, but we had a lot of questions about what was possible. The main problem was how to set up the balances and how to define electron donor(s) and C-source. Professor Heijnen gave very clear explanation of the issues involved and after the visit we were convinced that it was possible to produce PHB from syn-gas by fermentation. He also advised us on the reactor type to use. Syn-gas fermentation is gas-liquid mass transfer limited and thus a reactor which guarantees high mass transfer is necessary. His advice was to design a monolith reactor as is described in this report. In summary, Heijnen took away a lot of uncertainties surrounding the application of a syn-gas fermentation.

8-6 Interview with prof.dr. J.A. Moulijn

Prof. Moulijn is head of the section Reactor & Chemical Engineering, department Delft Chem Tech, Delft University of Technology

While designing the gasifier, we decided to consult prof. Moulijn, renowned for his knowledge about (oil) refineries and other process technological plants.

At the time of the interview, the major part of the Aspen model had already been finished and was presented to him, together with some results. Then, we asked his opinion of the results.

Prof. Moulijn thought that the model was quite good (in building the flowsheet, but also in choosing the right models to simulate wood). We discussed the products that came out and eventually decided to add ethane and pyridine, but they could be neglected as their fractions were undetectably low. Prof. Moulijn also advised to skip the drying step, as the reaction would be performed with steam.

Furthermore, he stressed that Aspen only gives the thermodynamic and thus theoretical values and that it still was very necessary to make a kinetic model.

The conversation focused on the amount of oxygen present in the reaction. Biomass contains oxygen, air and water too. Apparently the amount of air needed for producing syn-gas could be extremely low; biomass contains 3/4 oxygen for every C present. However, feeding oxygen provides heat energy for the endothermic gasification and pyrolysis reactions.

Further he advised us to speak with his assistant professor ir. W. de Jong.

8-7 Visit to Ajay Galdhar, Christian Peineke

The stream of dried particles requires processing in a solid/gas separation unit to yield a solid stream suitable for melting. Initially a cyclone was considered for this purpose. However a cyclone is not able to separate a stream of particles of 600 nm diameter. An alternative was to use a filter, however the small particle size would quickly block the filter and it is less than clear how the solid could be recovered from the filter.

It was decided to approach an expert at the section for particle technology to discuss alternatives and also to gain expertise on the processing of polymer aerosols.

8.7.1 Aerosol properties associated with polymer aerosols

Polymer aerosols have a number of remarkable properties. The particles are insulators and can accumulate a significant charge as they pass through pipes. This can result in them becoming ‘sticky’. For this reason the experts advised using pipes which are a short as possible to reduce the risk of this behaviour leading to problems. This problem becomes worse as particle concentration increases. A technique which can be used to reduce the problem is to use ionized air.

This behaviour does suggest that the particles can be encouraged to agglomerate which would make the use of a cyclone possible.

8.7.2 Equipment options

The experts said that cyclones can be used to remove particles down to a size of 1 micron, hence 600 nm particles might also be removed, albeit with a lower efficiency. However this was not a problem as the vapour would be recycled internally. Hence a cyclone could be usable, especially if agglomeration resulted in particles with a larger diameter.

However the experts suggested that if a cyclone did not work then a suitable unit might be an impactor. An impactor utilises the difference in inertia between the gas and the solid to precipitate the particles from the aerosol.

8.7.3 Finding further information

The experts recommended the book ‘Aerosol technology’ by Hinds [1999] as an excellent resource for designing the final unit. The company Simco was also recommended as a source for equipment suitable for the application in mind.

8-8 Visit to Prof. Kapteijn

Professor Kapteijn is professor in catalysis at the section reactor and catalysis engineering at the TU-Delft.

The objective of the visit to Kapteijn was to discover if there were alternative routes to produce methanol, or any liquid substrate suitable for fermentation, from syn-gas without needing to purify the syn-gas first. Micro-organisms are often heterotrophs and therefore a high methanol purity was not of great importance. The objective was to find a robust catalyst, which could deal with high levels of impurities.

Kapteijn's suggestion was to look at direct biomass liquefication as methanol synthesis does require a high purity feed.

This was investigated immediately after the meeting and found to result in a mixture, which was extremely unsuitable for fermentation. The bio-crude contains a large amount of components which would either be toxic to the bacteria or which they would leave unconverted.