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Production of adipic acid from forest residues

Modelling and investigation of the downstream process in Aspen Plus

Master's thesis in Sustainable Energy Systems

Henrik Wahnström

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2017

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Abstract

Within the chemical industry fossil resources are commonly used as raw material for producing desired chemicals. Due to that fossil resources are a finite resource and that using these resources result into CO_2 emissions that have an environmental impact there is an eager to find new alternative production method within the chemical industry. Lignocellulosic, plant biomass, is seen as a promising renewable feedstock that could replace the current fossil feedstock used in the chemical industry.

In this present work an alternative manufacturing process of adipic acid is investigated. Adipic acid is a chemical which plays an important role in the production of nylon. The most common commercial way to produce adipic acid today is by using benzene originated from crude oil as a feedstock. In this work an alternative method where adipic acid is produced from glucose that originates from lignocellulosic is being investigated. Focus in this work have been to study the downstream process where the separation of adipic acid from the process stream is carried out.

The downstream process has been designed in Aspen Plus and a feasible solution for extracting adipic acid is presented. Different byproducts that could interfere with the separation process have been investigated. A scenario analysis was carried out where the impact of an increased amount of byproducts was studied. No impact on the feasibility of the process was noticed. The results of the model has been compared with a previously made thesis with in this area from a production and energy demand point of view.

Keywords: Adipic acid, Forest residues, Lignocellulosic, Aspen Plus, Downstream process

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Henrik Wahnström, Gothenburg, February 2017

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1
Introduction

Today's society is facing several challenges. One is to reduce our dependency on fossil fuels in order to achieve a more sustainable society. To meet this challenge alternative solutions have to be found in those areas where we today use and rely on fossil resources. In the chemical industry fossil fuel is commonly used as a raw material to produce desired chemicals. A possible way to address this problem would be to find a method to use renewable resources such as biomass for the same purpose.[1]

Sweden is seen as a forest rich country and the forest industry is one of the most important industries in Sweden. In 2015 Sweden was the third largest exporter of pulp, paper and sawn wood products.[2] However for the forest industry in Sweden to stay competitive in the future market, research within new areas of more advanced products and processes needs to be done. Utilizing forest residues for chemical production could be considered a promising way for the forest industry to stay competitive in the future.[1]

BioBuF is an ongoing interdisciplinary project at Chalmers which studies the potential to replace petroleum based resources with renewable resources from a technical, systems integration and environmental point of view. Focus of the project is the simultaneous production of the basic and fine chemicals integrated in a biorefinery concepts where microalgae, forest residues and municipal solid waste are considered as a renewable resources. Within this project an alternative manufacturing process of the platform chemical adipic acid is being investigated.[3]

1.1 Biomass

According to EU renewable directive biomass is defined as
the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste;[4]

The benefit with biomass is that it has the potential to be a CO_2 neutral alternative, as the carbon dioxide that is released during combustion is then tied up during photosynthesis to produce new biomass. In that case a closed cycle is achieved and the net CO_2 level in the atmosphere can be assumed to be constant.[5]

1.2 Biorefinery

A biorefinery can be described as a facility that uses biomass to extract desired end products, such as energy, bio-material and chemicals. The main difference between a petroleum refinery and biorefinery is thus the feedstock that is used in the process.[5]

Biorefinery can be categorised into three different phases of development. Phase 1 biorefinery is defined as a facility that uses one certain kind of bioresource to produce one major product. This kind of biorefineries have fixed process parameters and have been shown to be economically feasible. The pulp and paper industry is one example of a phase 1 biorefinery.[6]

Phase 2 biorefinery is also using one specific resource but its process is more flexible and can produce several difference major products. This gives the possibility to produce according to a varying demand portfolio which increases the competitiveness of the refinery. The possibility to upgrade a phase 1 refinery to a phase 2 can be a promising alternative e.g. for existing pulp and paper industry to increase its competitiveness. One example of a phase 2 biorefinery is the Roquette site of Lestrem in France where several different products such as polyols, protein and derivatives, cereal sugar, organic acid are produced using cereal grains as a resource.[6]

The most advance refinery is denoted as phase 3. It is not today commercially feasible but there is a lot of ongoing research within this area. The phase 3 refinery is similar to phase 2 in that sense that it can produce several end products but it can also use different kind of resources as feedstock. This gives the refinery a lot of possibilities to vary different combinations of feedstock and end products in order to maximise the profit. A biorefinery that use lignocellulosic biomass as a feedstock and utilizing both the polysaccharides (cellulose and hemicellulose) and lignin is one example of how a phase 3 refinery can be constructed. Other feedstock that could be used is whole crop, green and marine resources.[6]

1.3 Lignocellulosic feedstock

Lignocellulosic feedstock refers to plant biomass consisting of cellulose, hemicellulose, lignin and extractives. The lignocellulosic feedstock is seen as a very promising future material from which chemicals and biofuels could be produced. A great benefit with lignocellulosic feedstock is its abundance from global perspective, which makes it to a cheap and accessible resource. Lignocellulosic is also seen as a second order resource which does not compete with the food market. On the contrary to the first generation resources, where the cultivation of glucose-rich crops such as sugar-cane and corn can be seen to compete with conventional food cultivation which could result into higher grain prices.[5]

Lignocellulose has a complex structure in which cellulose is the main component. Cellulose is a polysaccharide consisting of glucose molecules. Hemicellulose is also a

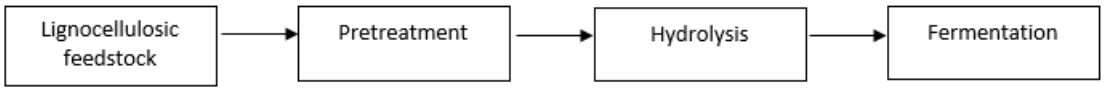

Figure 1.1: the conversion route for producing fine chemicals through fermentation

polysaccharide but differ from cellulose as it is more branched and it also contains several other monosaccharides in addition to glucose such as xylose, galactose, mannose and arabinose. Lignin is an amorphous polymer that is highly branched. The lignin has the function to work as a glue that bind together the long polysaccharides and gives the tree its mechanical strength.[7]

Due to lignocellulosic stable structure pretreatment is needed to make the feedstock suitable for conversion. The purpose with the pretreatment is to break down, fractionate the main components and thereby make it more suitable for conversion. An illustration of how the process of producing fine chemicals from lignocellulosic feedstock can be seen in figure 1.1. The first step involves a mechanical pretreatment which breaks down the structure and decrease the size of the particle to increase the surface area. The mechanical pretreatment is followed by a chemical pretreatment, hydrolysis. The hydrolysis can be taken place in an acid or alkali environment and the purpose with this pretreatment step is to separate the different main components (cellulose, hemicellulose and lignin). The pretreatment step is then followed by an additional hydrolysis to produce fermentable sugars and a fermentation step to produce the final desired chemical.[6]

1.4 Adipic acid

Adipic acid ($C_6H_{10}O_4$) is a dicarboxylic acid and is commonly used in the chemical industry. The molecule structure of adipic acid can be seen in figure 1.2. Adipic acid can be found in the nature, for example in the sugar beet, but for industrial use synthetically produced adipic acid is used. Synthetic adipic acid was first produced in 1902, but only in small scale. In 1935, DuPont began to produce nylon 6,6 by using adipic acid making adipic acid a very important chemical. Today adipic acid is still primarily used for producing nylon where around 90% of the produced adipic acid is used. It has also other applications such as a flavorant and gelling agent.[8]

The most common commercial way today to produce adipic acid is by using benzene from crude oil according to the figure 1.3. This method was originally developed by DuPont in 1940 but has been modified during the years. Benzene is in a first step reduced to cyclohexane by hydrolysis. Thereafter the cyclohexane is converted by oxidation to a mixture of cyclohexanol and cyclohexanone. At the last step, adipic acid is produced in the presence of nitric acid. During this step byproducts such as N_2, NO, NO_2 and N_2O are formed. These NOx-emissions have a negative impact on the climate, in particular to global warming potential.[9] For example compare

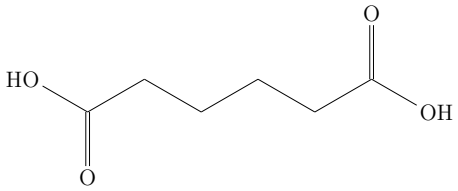

Figure 1.2: the molecule structure for adipic acid

to CO_2 the N_2O has an estimated 310 greater global warming potential.[10]

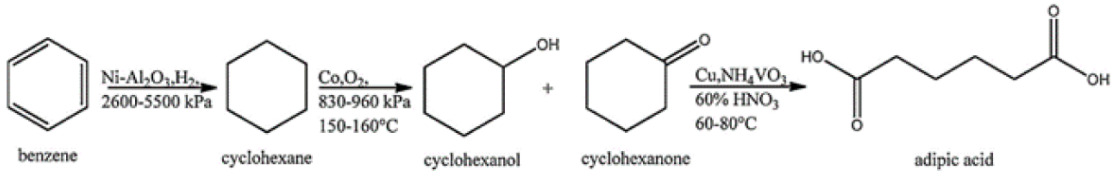

Figure 1.3: the production route of adipic acid from benzene.[9]

Due to that benzene is a fossil resource and that the current most common production route for adipic acid results into large NOx-emissions, alternative productions methods are being investigated. One alternative production method can be seen in figure 1.4. Glucose that originates from biomass is used as a feedstock instead of benzene. By fermentation where microorganism convert sugars into desired products in an oxygen poor environment adipic acid is produced. When producing adipic acid lysine is first formed as an important intermediate step[13][14].

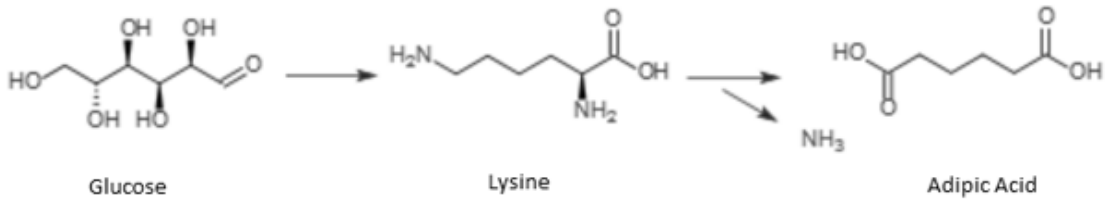

Figure 1.4: the production route for adipic acid by fermentation.[13][14]

1.5 Motivation of thesis

In this work a bio based production route for adipic acid is being investigated. Focus in this work is to study the downstream process which separate the adipic acid from the process stream. For simulating the downstream process the software Aspen Plus has been used and the model has been designed on the basis of a previously made thesis work [11]. Important process parameters that was taken into account when designing the model was a high purity of the extracted adipic acid and low amount

of losses of the adipic acid in the process. A challenge for designing the process was to detect possible compounds that could occur and interfere with the feasibility of the process. The solubility of the different detected compounds was investigate to study if they could interfere the purity of the extracted adipic acid.

In chapter 2 the methods and models that have been used in this work are presented as well as scenarios for assessing the impact of co-produced impurities. In chapter 3 the results for the produced adipic acid and scenario analysis is being evaluated. Conclusions and ideas of future work within this topic is presented in chapter 4.

2
Method and Model description

The aim of this project is to study the manufacturing process of adipic acid from forest residues. In this project GROT (abbreviation for branches and tops in Swedish) is used as feedstock to the process. The pretreatment which fractionates GROT into its main components (cellulose, hemicellulose, lignin and extractives) will not be further investigated in this project. Instead focus will be put on the fermentation of glucose to adipic acid and the downstream process which separate adipic acid from the fermentation broth.

2.1 Model description

For modelling and simulating the process the software Aspen Plus has been used and a simplified flowsheet over the designed process can be seen in figure 2.1. The model has been designed on the basis of an earlier thesis work [11] and a complete flowsheet of the designed model can be found in appendix A.5. The first part of the model in the flowsheet describes the fermentation part. This part is not rigorously modeled. Instead inlet and outlet streams are based on literature data for conversion, selectivities and mass balances; reaction kinetics microbial growth etc. are not part of the model. The second part of the model describes the downstream process of the model which describes the separation of the adipic acid from the fermentation broth. This part is described in a more rigorous model compare to the fermentation part and investigating the downstream part of the model have been the main focus in this work.

2.1.1 Fermentation part

The inflow stream to the process is derived from the GROT and its composition is determined from [12] and can be seen in table 2.1. This inflow stream is assumed to be the results of a chemical pretreatment of GROT, where lignin and extractives have been removed. The remaining cellulose and hemicellulose is assumed to enter the process. Water is thereafter added to the process to achieve a 40mM glucose solution according to [13].

For the fermentation process two different microorganisms can be used, Corynebacterium glutamicum and Saccharomyces cerevisiae. Both of these organisms are used

to convert glucose into adipic acid where lysine is assumed to be formed in an intermediate step. Different byproducts that can occur differ depending on which microorganism has been used and from this knowledge two different base scenarios were designed and can be found in table 2.2. The two defined base scenarios will be explained in more detail in section 2.2.

Table 2.1: The composition of the inflow stream which originates from cellulose and hemicellulose which is extracted from GROT.

$Compounds$	$Molecule formula$	$Amount[kmole/hr]$
Fucose	C6H12O5	0,005330166
Arabinose	C5H10O5	0,151535336
Rhamnose	C6H12O5	0,010660331
Galactos	C6H12O6	0,150560613
Glucose	C6H12O6	1,748445826
Xylose	C5H10O5	0,343868647
Mannose	C6H12O6	0,412827487
Galacturonic acid	C6H10O7	0,076619965
Glucuronic acid	C6H10O7	0,036056454

Assumptions Fermentation

- Two microorganisms, Corynebacterium glutamicum and Sacchromyces cerevisiae, are used for the two different scenarios
- The input stream to the process is assumed to consist of cellulose and hemicellulose
- Water added to achieve 40 mM glucose solution
- Fermentation temperature is set to be 37°C
- Glucose is converted to adipic acid where lysine is formed as an intermediate step, see figure 1.4
- The conversion rate was set to be 30.9% for glucose to lysine and 50% for lysine to adipic acid

2.1.2 Separation part

For the separation part a multi-effect evaporation system with four evaporators in series are used to separate the water from the process stream. The benefit by using several evaporators that are connected in series, where the pressure is reduced stepwise, is that the vapour produced in the first evaporator can be used to supply energy demand in the next evaporator. Thereby the total requirement for energy demand can be supplied by adding high pressure steam to the first evaporator and thereafter heat exchange the extracted vapour. How great the energy demand is for the different evaporators depends on the operating pressure and chosen vapour fraction. High pressure and vapour fraction enables to reduce a large amount of water, but it will increase the cost for equipment and steam. An increased amount of

vapour that leaves the system also increases the potential of losses of adipic acid in the vapour phase. Therefore it is important to investigate the content of the vapour phase to prevent possible losses of adipic acid. For heat exchanging ΔT_{min} is set to be 10°C. After the evaporators the process stream enters the cooling crystallization system which reduce the temperature down to 10°C. This enables the adipic acid to precipitate from the rest of the solution and filter it to extract the adipic acid in solid state. The water amount that enters the crystallizer and the crystallization temperature determine which compounds precipitate and in what amounts. Therefore the solubility for the different compounds that could occur in the process was investigated. The main outcome from this investigation was that the small amounts and/or relatively high solubilities, no compound was found to precipitate under these conditions. The solubility data that has been used in the project can be found in appendix B. A certain amount of the filtrate is recycled back and mixed together with the output of the reactor. This is done to recover some adipic acid that still is dissolved to the stream. A detail flowsheet over the process and the chosen design parameters can be found in appendix A.

Assumptions Separation

- A multi-effect evaporation system is used
- For heat exchanging ΔT_{min} is set to be 10°C.
- Operating parameters for the crystallizer 10°C and 1 bar
- Only adipic acid is precipitating in the crystallizer
- Solubility data for adipic acid is taken from [15]

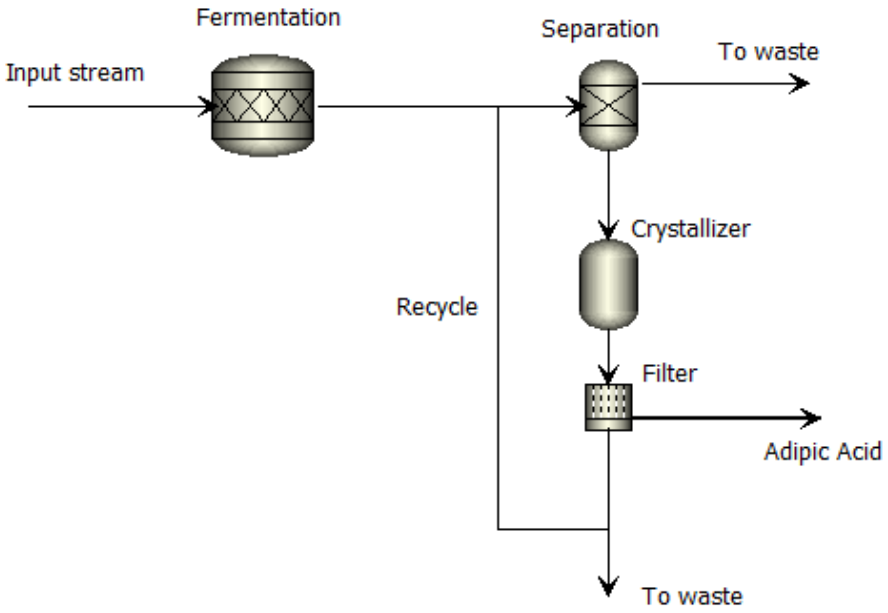

Figure 2.1: shows a simplified process over the designed process

2.2 Scenario set up

For the fermentation part two different base scenarios were constructed depending on which microorganism was used. The inlet stream for both base scenarios is the same and also the conversion rate from glucose to adipic acid with lysine produced in an intermediate step is set to be the same. For the base scenario 1 the byproducts were determine according to [13], where the microorganism Corynebacterium glutamicum is used. For the microorganism Saccharomyces cerevisiae from which the base scenario 2 is defined no published literature has been used. This base scenario was set up by given data from the BioBuF project at Chalmers Technical University. The data contained information of possible compounds that could occur. The total amount of byproducts was assume to be equal from a carbon content point of view between the scenarios. The amount of different compounds for scenario 2 were then estimated by balance the amount of carbons that the different compounds contained. Compounds that contained fewer carbons were assumed to occur more often compared to with compounds that had a greater carbon content. The formula used for estimating the amount of compounds can be seen below and an example of calculating the amount of glycerol is presented,

$$\frac{T}{B} * \frac{1}{C} = \frac{3,27}{8} * \frac{1}{3} = 0,136 \quad kmole/hr$$

where T is the total amount of carbon for the byproduction, B equals the number of different byproducts and C is the amount of carbon in the different byproducts. The composition for the both base scenarios can be seen in table 2.2.

To investigate the byproducts effect at the downstream process, the conversion rate of lysine to adipic acid was reduced. The conversion rate was initial set to be 50% according to [14]. This rate was reduced to 49, 45, 40 and 25%. The rate reduction was made by assuming an increased amount of the different byproducts. Due to that no specific data of the kinetics of the different reactions were given the amount of the increased production of byproducts were decided randomly. This was done by generating a matrix with random numbers between 0 and 1, where each number corresponded to a certain byproducts. The numbers were then used to calculate the additional amount produced moles, x_{new}, where the total weight and number of carbons molecules could not exceed the weight and carbon content corresponding to the reduction of lysine. The route mean square method was used to minimise the difference between the random generated numbers and the calculated x_{new}. An example for the calculation procedure is presented in table 2.3.

Assumptions Scenario set up

- Conversion rate lysine to adipic acid was reduced from 50% to 49, 45, 40 and 25%
- Increased amount of byproducts was determined randomly

Table 2.2: shows the composition for the base scenario 1 and 2 where the microorganism Corynebacterium glutamicum respective Saccharomyces cerevisiae is used. The total amount of glucose that enters the fermentation is 1.748 kmole/hr which corresponds to 315 kg/hr

Compound	*Scenario*1	*Scenario*2
$MoleFlow[kmole/hr]$		
Glucose	0,540	0,540
Lysine	0,332	0,332
Alanine	0,001	-
Glycine	0,019	-
Dihydroxyacetone	0,203	-
Glycerol	0,012	0,136
Trehalose	0,007	-
Acetate acid	0,074	0,204
Pyruvic acid	0,001	-
Lactic acid	0,037	0,136
Butyric acid	-	0,102
Succinic acid	-	0,102
Carbondioxid	-	0,408
Ethanol	-	0,204
2-oxoglutaric acid	-	0,082
Adipic acid	0,332	0,332
Ammonia	0,332	0,332

Table 2.3: scenario set up for scenario 1 in which a reduction to a 40% conversion rate is made

compounds	*random*	x_{new}	$diff$	*carbon*	*weight*
Alanine	0,495924897	0	0,245941504	0	0
Glycine	0,179850026	0	0,032346032	0	0
Dihydroxyacetone	0,514766687	0	0,264984743	0	0
Glycerol	0,291353087	0	0,084886621	0	0
Trehalose	0,976195842	0	0,952958321	0	0
Acetic acid	0,828885432	0,161534547	0,445357204	3,877	9,700
Pyruvic acid	0,067409258	0	0,004544008	0	0
Lactic acid	0,627295256	0	0,393499338	0	0
			2,424517771	3,877	9,700

3

Results and Discussion

Under this section the results of the production of adipic acid is presented. The energy demand per kg of produced and extracted adipic acid is first estimated for both scenarios. The results are compared with the previously made thesis [11] that has been used in this work. Then, the impact of varying amounts of byproducts is investigated.

3.1 Adipic acid production

The production of adipic acid in the process for the both base scenarios can be seen in table 3.1. The total inflow of glucose to the process is equal to 315 kg/hr and the produced amount of adipic acid is determined to be 48,5 kg/hr which gives a conversion rate of 15,4 wt%. This value is the same for both base scenarios. However it is not possible to extract all of the adipic acid in the filter. A certain amount of adipic acid is still soluble in the process stream that enters the filter and therefore is not able to be extracted. The energy demand for the process, which is determined from the first evaporator, is roughly the same for the two base scenarios 16,57 respective 16,59 MW and this corresponds to approximately 1,23 GJ/kg produced adipic acid.

The high energy demand in the process is due to that the water content is reduced by evaporation which demands a lot of energy. In figure 3.1 the energy demand for the different components can be seen in a bar chart. The total energy demand for the process without heat exchanging is determine to be roughly 33 MW and by heat exchanging the energy demand is reduced by half to 16,5 MW. The separation part consist of Evap 1 to Evap 4 and as can be seen in figure 3.1 this part of the process is dominating the energy demand. In order to improve the profitability of the plant the separation part should be further investigated. For the current design and chosen parameters there is still room for improvements to reduce the losses in vapour phase.

Table 3.1: the results for the production of adipic acid for the two different scenarios. The energy demand corresponds to energy duty for the first evaporator.

Parameter	Scenario 1	Scenario 2
Produced Adipic Acid	48,52 [kg/hr]	48,52 [kg/hr]
Extracted Adipic Acid	46,52 [kg/hr]	46,58 [kg/hr]
Wasted Adipic Acid	1,98 [kg/hr]	1,93 [kg/hr]
Energy Demand	16,57 [MW]	16,59 [MW]

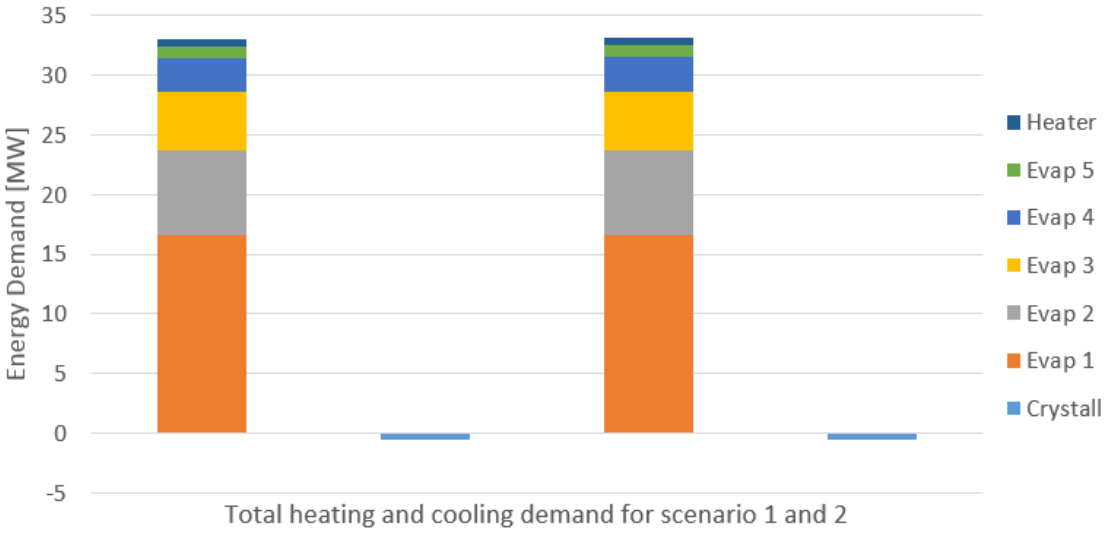

Figure 3.1: heating and cooling demand for the process

Another way to reduce the energy demand in the separation part and thereby increase the profitability of the process plant would be to lower the amount of water which enter the process. The current chosen concentration of glucose is set to 40mM and this value is taken from [13]. This reference has been used in a previously thesis work [11]. Data that has been constructed in this thesis work together with values from this current work is presented in table 3.2. From table 3.2 it can be seen that the conversion rate glucose to adipic acid is similar in both work, 15,4 compare to 20,8 wt%. However the water content in the two processes differ greatly. From a 0,7 to 7 wt% concentration of glucose, which corresponds to a 40mM respective 400mM glucose solution. As mentioned previously evaporation of the water in the separation part is very energy demanding and this can be seen as the main reason for the great difference between the produced adipic per energy demand.

Results Adipic Acid Production

- Total conversion rate of 15,4 wt%
- The separation part is dominating the energy consumption
- Losses of adipic acid in vapour phase can be neglected

Table 3.2: comparing data from a previously thesis work[11] with values from this report.

	Scenario 1	Comparing work [11]
Water	43710 [kg/hr]	8730 [kg/hr]
Glucose	315 [kg/hr]	630 [kg/hr]
Adipic Acid	48,5 [kg/hr]	131 [kg/hr]
Conversion rate	15,4 wt%	20,8 wt%
Energy demand	16,57 [MW]	0,91 [MW]
Energy demand per produced adipic acid	1,23 GJ/kg$_{AA}$	0,025 GJ/kg$_{AA}$

3.2 Scenario analysis

A scenario analysis was carried out to investigate the impact of an increase amount of byproducts. This was done by reducing the conversion rate and increasing the corresponding amount of byproducts randomly. The results from the reduced conversion rate can be seen in figure 3.2. The total energy demand for the different scenarios is almost the same as the total water content in the process remained the same. A reduction between 0 and 10 percentage point indicates a straight increasing line for the energy demand per produced amount of adipic acid as the conversion rate is reduced. For a greater reduction of 25 percentage point, which can be seen as an extreme case, an increased inclination can be noticed. The change can be described to be exponential as the energy demand for the process is roughly the same but the produced adipic acid is decreasing as the conversion rate is reduced. When the conversion rate is reduced by 50 percentage point the produced amount of adipic acid will be zero and the energy demand per kg produced adipic acid will go to infinity. Plotting the extracted adipic acid a similar pattern can be seen, however here the energy demand is a bit higher due to that there is a reduction of adipic acid due to the losses in the system.

An increased amount of byproducts could interfere with the feasibility of the model. The model contain a recycle stream to recover adipic acid that is still dissolved in the stream. However the recycling can also results into an increased concentration of the byproducts and could cause problem with the feasibility of model. For the current chosen design parameters for the process no such impact has been noticed.

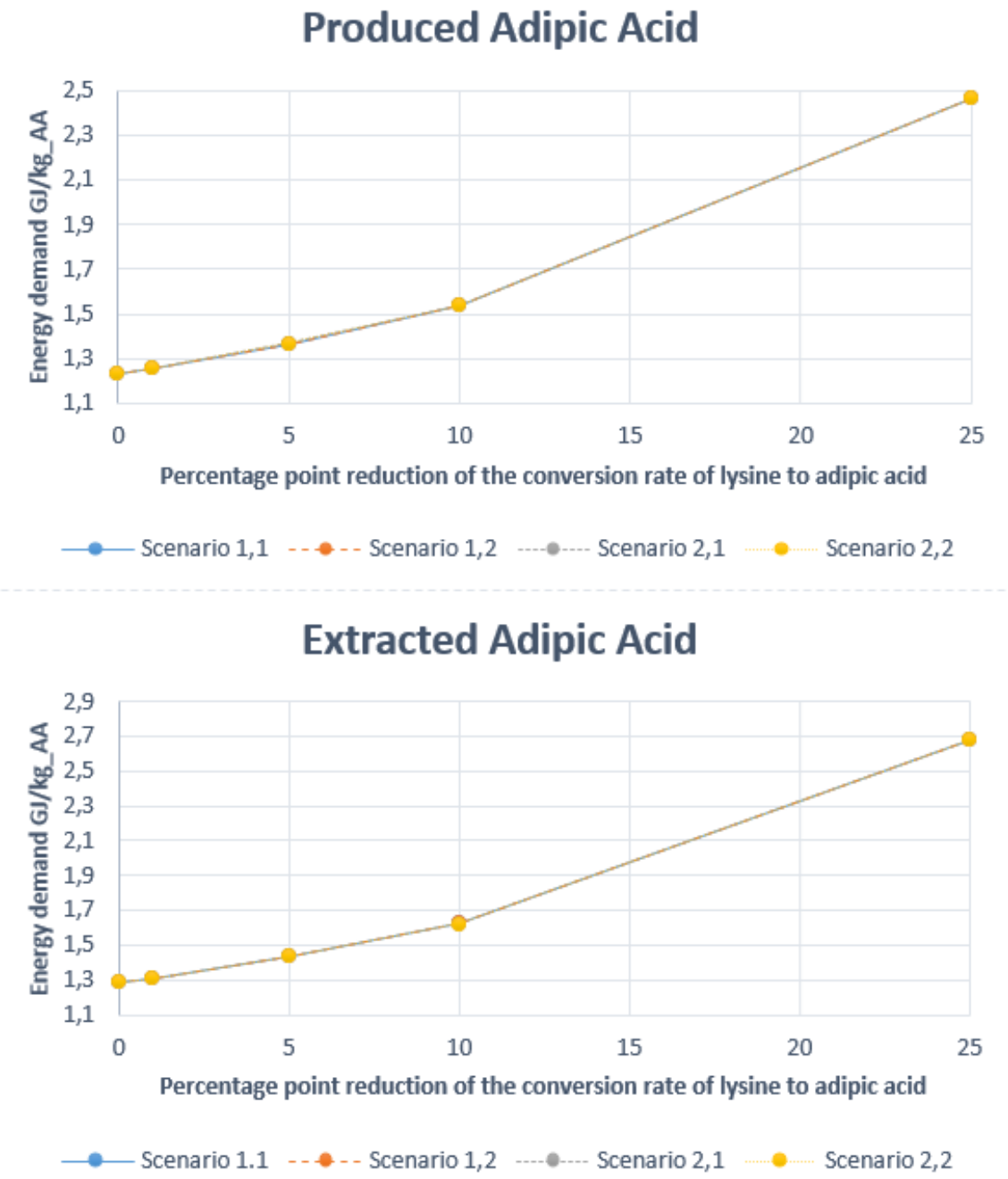

Figure 3.2: presents the results for the reduce conversion rate of lysine to adipic acid.

Results Scenario Analysis

- Reduce conversion rate increases the energy demand per kg produced adipic acid
- Increased amount of byproducts have no noticed impact on the feasibility of the process

4
Conclusion

An alternative production method for adipic acid has been investigated. The alternative production method offer a way of producing adipic acid from glucose extracted from renewable resources such as GROT instead of benzene originated from crude oil.

4.1 Process conclusion

The process present a solution for producing adipic acid from GROT. The total conversion rate from glucose to adipic acid is estimated to be 15,4 wt%. Due to the high water content that originates from the fermentation process the separation part has a high energy demand, 1,23 GJ/kg produced adipic acid. To reduce the losses of adipic acid a certain amount of the filtrate is recycled back and mixed together with the output from the reactor. For the current designed system a ratio of 0,9 is chosen and this results into 4% losses of adipic acid in the process. A higher value would lower the losses further but it could also interfere with the feasibility of process as it would increase the concentration byproducts in the process. The scenario analysis that was carried out by increasing the impact of an increased amount of byproducts gave no notice impact of the feasibility of the model.

4.2 Outlook

For the manufacturing process of adipic acid two main areas for improving the cost and environmental benefit have been noticed. Firstly the energy demand in the separation process is highly dependent on the amount of water that needs to be evaporated in order to precipitate the adipic acid. The water content for the process originates from the fermentation part where the glucose concentration is set to be 40mM, which is based on one reference. A lower amount of water in the process would have an impact on the concentration of glucose in the fermentation area, but no investigation of how the conversion rate would be affected have been done in this work. However a reduction of the water amount would lower the energy demand in the separation part. Secondly for the fermentation part the conversion rate from glucose to adipic acid is set to be 15,4 wt%. This can be seen as a rather low number. In order to improve the feasibility of the process this conversion rate should be investigated and the possibilities to increase the yield of adipic acid. In

this work it has been assumed that the two different microorganisms that have been investigated have the same conversion rate. Choosing a microorganism with a high conversion rate would be beneficial for the adipic acid production. However it is also important to investigate what byproducts are produced and how they interfere with the separation process.

For the current process only the fermentation and separation of the adipic acid has been investigated. The effect of the pretreatment of lignocellulosic which fractionates the feedstock into its main components (cellulose, hemicellulose, lignin and extractives) has not been investigated in this work. However this process step is an important part for this alternative manufacturing process. Therefore it would for a future work be interesting to study how this can be done in an efficient way from an economic and environmental perspective.

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A

Appendix 1

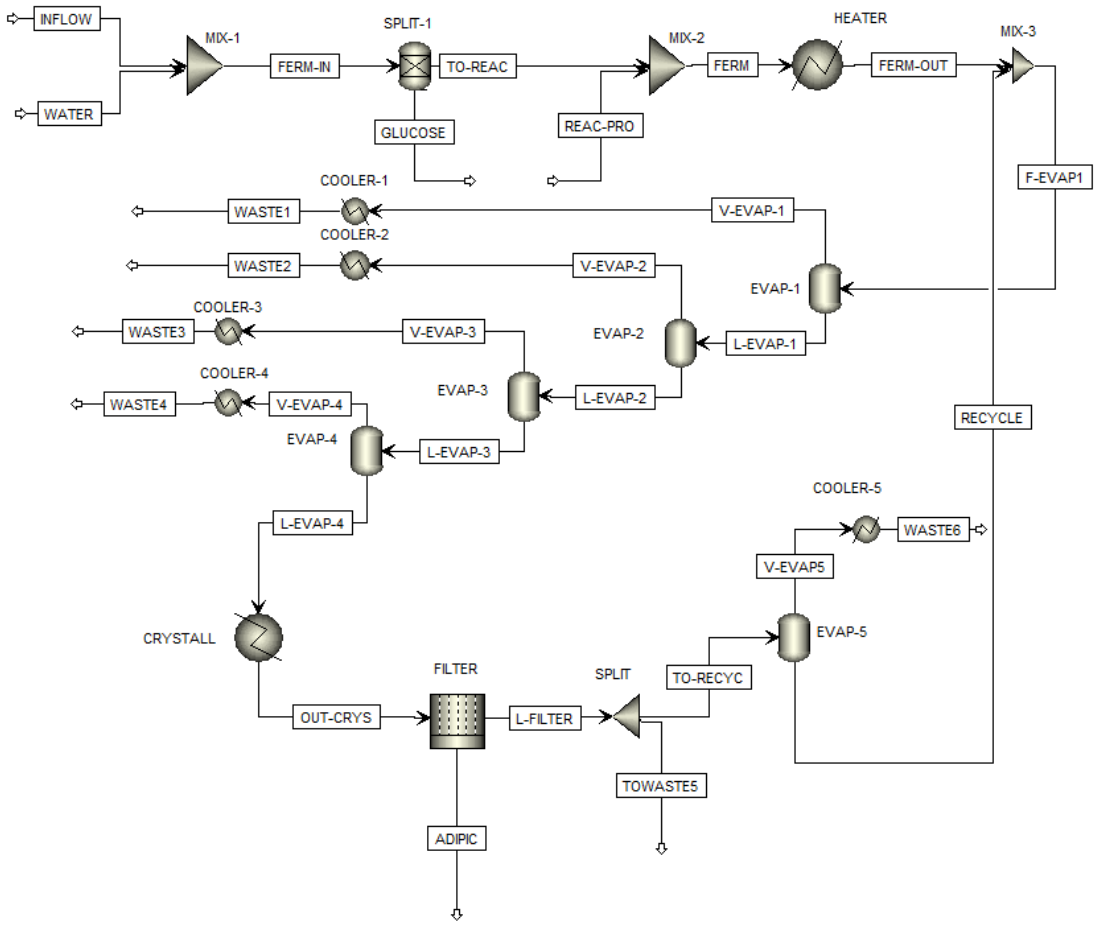

Figure A.1: flowsheet of the designed model in Aspen Plus

Table A.1: Parameters for the process units. Bold marked indicates chosen parameters for the process

ProcessUnit	$T[C]$	$P[bar]$	Additional information
HEATER	37	1	
EVAP1	180	**10**	**v=0.35**
EVAP2	169	**7.5**	**v=0.45**
EVAP3	154	**5**	**v=0.55**
EVAP4	133	**2.5**	**v=0.65**
EVAP5	111	**1**	**v=0.5**
CRYSTALL	**10**	**1**	
FILTER	10	1	
SPLIT	10	1	**split ratio = 0.9**

Table A.2: the composition of the process stream for the base case scenario 1

Substream: MIXED	FERM-OUT	RECYCLE	ADIPIC	WASTE1
Mole Flow kmol/hr				
WATER	2426,337	34,32477	0,000851386	868,7912
ARABINOS	0,1515351	1,360695	1,31E-05	8,60E-05
GALACTOS	0,1505604	1,354863	1,31E-05	2,36E-06
GLUCOSE	0,54	4,858844	4,69E-05	3,97E-05
XYLOSE	0,3438681	3,0878	2,98E-05	0,000194208
MANNOSE	0,4128268	3,714948	3,58E-05	6,47E-06
LYSINE	0,332	2,963307	2,86E-05	0,000657103
ALANINE	0,001	0,0090049	8,69E-08	9,36E-83
GLYCINE	0,019	0,1709584	1,65E-06	2,40E-06
DHA	0,203	0,4780622	4,78E-06	0,0206001
GLYCEROL	0,012	0,0995671	9,61E-07	0,000183661
TREHALOS	0,007	0,0629341	6,07E-07	1,94E-06
S-ACETAT	0,074	0,00474636	8,53E-08	0,0177446
PYREVATE	0,001	0,00061133	6,93E-09	0,000139352
LACTATE	0	5,12E-07	4,94E-12	0
S-ADIPIC	0,332	0,1219305	1,18E-06	3,07E-05
ACETATE	0	0	0	0
ADIPIC	0	0	0	0
NH3	0,332	1,30E-05	1,67E-09	0,2235992
H+	0	0	0	0
ADIPICS	0	0	0,3183399	0
S-BUTRAT	0	0	0	0
BUTYRATE	0	0	0	0
H-SUC-01	0	0	0	0
LACTIC	0	0	0	0
S-LACTIC	0,037	0,1579132	1,54E-06	0,00334489
CARBO-01	0	0	0	0
ETHANOL	0	0	0	0
S-SUCCIN	0	1,57E-10	1,52E-15	5,67E-14
RHAMNOSE	0,0106603	0,0954046	9,21E-07	1,52E-05
GALAACID	0,0766198	0,6894874	6,65E-06	1,57E-06
GLUCACID	0,0360563	0,3244645	3,13E-06	7,41E-07
OXO	0	1,01E-10	9,74E-16	5,59E-14
FUCOSE	0,00533016	0,0457512	4,42E-07	5,57E-05
Total Flow kmol/hr	2429,415	53,92608	0,3193806	869,0579
Total Flow kg/hr	44142,68	3847,971	46,56967	15658,74

Table A.3: the composition of the process stream for the base case scenario 1

Substream	WASTE2	WASTE3	WASTE4	TOWASTE5	WASTE6
Mole Flow kmol/hr					
WATER	726,1479	488,1479	279,5429	9,802983	53,90208
ARABINOS	8,57E-05	7,42E-05	7,23E-05	0,1511898	1,39E-05
GALACTOS	2,01E-06	1,41E-06	1,02E-06	0,1505403	1,37E-07
GLUCOSE	2,78E-05	1,45E-05	6,53E-06	0,5398716	4,90E-07
XYLOSE	0,000193548	0,000167395	0,000160471	0,3430922	3,02E-05
MANNOSE	5,50E-06	3,84E-06	2,69E-06	0,412772	3,46E-07
LYSINE	0,000681755	0,000629643	0,000676769	0,3292727	0,000147459
ALANINE	1,83E-82	3,96E-82	1,45E-81	0,00100054	1,36E-81
GLYCINE	2,33E-06	1,98E-06	1,88E-06	0,0189954	3,51E-07
DHA	0,0265526	0,0324577	0,0505541	0,055089	0,0177389
GLYCEROL	0,000208128	0,000213507	0,00026085	0,0110701	6,39E-05
TREHALOS	2,01E-06	1,87E-06	2,06E-06	0,00699273	4,76E-07
S-ACETAT	0,0188426	0,0172277	0,0151061	0,000982488	0,00409603
PYREVATE	0,000175195	0,000206513	0,000292425	7,98E-05	0,00010672
LACTATE	0	0	0	5,69E-08	0
S-ADIPIC	2,90E-05	2,28E-05	1,90E-05	0,0135481	3,05E-06
ACETATE	0	0	0	0	0
ADIPIC	0	0	0	0	0
NH3	0,0846896	0,0204632	0,0030688	1,92E-05	0,000159939
H+	0	0	0	0	0
ADIPICS	0	0	0	0	0
S-BUTRAT	0	0	0	0	0
BUTYRATE	0	0	0	0	0
H-SUC-01	0	0	0	0	0
LACTIC	0	0	0	0	0
S-LACTIC	0,00400234	0,00440654	0,00589758	0,017726	0,00162088
CARBO-01	0	0	0	0	0
ETHANOL	0	0	0	0	0
S-SUCCIN	6,34E-14	5,60E-14	5,63E-14	1,75E-11	1,13E-14
RHAMNOSE	1,52E-05	1,32E-05	1,27E-05	0,0106007	2,31E-06
GALAACID	1,09E-06	5,63E-07	2,47E-07	0,0766097	1,68E-08
GLUCACID	5,11E-07	2,65E-07	1,16E-07	0,0360516	7,93E-09
OXO	6,17E-14	5,23E-14	4,76E-14	1,12E-11	7,97E-15
FUCOSE	5,95E-05	5,63E-05	6,07E-05	0,00508487	1,26E-05
Total Flow kmol/hr	726,2834	488,2239	279,6191	11,98357	53,92608
Total Flow kg/hr	13087,28	8799,01	5042,29	535,6746	973,1004

Table A.4: the composition of the process stream for the base case scenario 2

Stream	FERM-OUT	RECYCLE	ADIPIC	WASTE1
Mole Flow kmol/hr				
WATER	2426,337	31,94489	0,000792065	868,6127
ARABINOS	0,1515351	1,360611	1,26E-05	8,62E-05
GALACTOS	0,1505604	1,354867	1,25E-05	2,37E-06
GLUCOSE	0,5399999	4,858777	4,48E-05	3,99E-05
XYLOSE	0,3438681	3,087613	2,85E-05	0,000194756
MANNOSE	0,4128268	3,714958	3,43E-05	6,49E-06
LYSINE	0,3319999	2,961708	2,73E-05	0,00065854
ALANINE	0	6,17E-10	5,69E-15	5,77E-90
GLYCINE	0	1,16E-08	1,07E-13	1,47E-13
DHA	0	2,62E-08	2,52E-13	7,94E-10
GLYCEROL	0,1361614	1,126744	1,04E-05	0,00208387
TREHALOS	0	4,19E-09	3,86E-14	1,17E-13
S-ACETAT	0,2042421	0,0123957	2,20E-07	0,048858
PYREVATE	0	0	0	0
LACTATE	0	0	0	0
S-ADIPIC	0,3319999	0,1186624	1,09E-06	2,99E-05
ACETATE	0	0	0	0
ADIPIC	0	0	0	0
NH3	0,3319999	1,20E-05	1,61E-09	0,2234012
H+	0	0	0	0
ADIPICS	0	0	0,3187102	0
S-BUTRAT	0,1021211	0,0566111	6,23E-07	0,0146647
BUTYRATE	0	0	0	0
H-SUC-01	0	0,000240529	2,22E-09	0
LACTIC	0	0	0	0
S-LACTIC	0,1361614	0,5703701	5,32E-06	0,0121493
CARBO-01	0,4084842	0	3,32E-12	0,4073491
ETHANOL	0,2042421	0,000345087	1,44E-08	0,1000515
S-SUCCIN	0,1021211	0,9051514	8,35E-06	0,000363728
RHAMNOSE	0,0106603	0,0953894	8,80E-07	1,52E-05
GALAACID	0,0766198	0,6894896	6,36E-06	1,58E-06
GLUCACID	0,0360563	0,3244655	2,99E-06	7,44E-07
OXO	0,0816968	0,7198302	6,64E-06	0,000445026
FUCOSE	0,00533016	0,0456852	4,22E-07	5,57E-05
Total Flow kmol/hr	2430,436	53,94882	0,3197056	869,4231
Total Flow kg/hr	44208,96	4075,326	46,62385	15680,43

Table A.5: the composition of the process stream for the base case scenario 2

Stream	WASTE2	WASTE3	WASTE4	TOWASTE5	WASTE6
Mole Flow kmol/hr					
WATER	726,3513	488,2906	279,6249	9,540222	53,91711
ARABINOS	8,63E-05	7,55E-05	7,72E-05	0,1511809	1,65E-05
GALACTOS	2,02E-06	1,44E-06	1,10E-06	0,1505408	1,69E-07
GLUCOSE	2,81E-05	1,50E-05	7,26E-06	0,5398642	6,44E-07
XYLOSE	0,000195	0,000170315	0,000171587	0,3430721	3,59E-05
MANNOSE	5,55E-06	3,92E-06	2,93E-06	0,4127732	4,28E-07
LYSINE	0,000686154	0,000639352	0,000718675	0,3290978	0,000172342
ALANINE	1,26E-89	2,71E-89	9,95E-89	6,86E-11	9,33E-89
GLYCINE	1,59E-13	1,36E-13	1,36E-13	1,29E-09	2,83E-14
DHA	1,47E-09	1,81E-09	2,89E-09	3,03E-09	1,08E-09
GLYCEROL	0,00237046	0,00245141	0,00312116	0,1252869	0,000837917
TREHALOS	1,35E-13	1,26E-13	1,45E-13	4,65E-10	3,66E-14
S-ACETAT	0,0519278	0,0475275	0,0418216	0,00265027	0,0114567
PYREVATE	0	0	0	0	0
LACTATE	0	0	0	0	0
S-ADIPIC	2,84E-05	2,27E-05	1,99E-05	0,0131851	3,59E-06
ACETATE	0	0	0	0	0
ADIPIC	0	0	0	0	0
NH3	0,0847639	0,0205468	0,00310555	1,94E-05	0,000162842
H+	0	0	0	0	0
ADIPICS	0	0	0	0	0
S-BUTRAT	0,0182307	0,0211739	0,0296019	0,00750604	0,0109432
BUTYRATE	0	0	0	0	0
H-SUC-01	0	0	0	2,67E-05	0
LACTIC	0	0	0	0	0
S-LACTIC	0,0145849	0,01617	0,0224337	0,0641188	0,00669961
CARBO-01	0,00113304	2,15E-06	3,05E-09	3,32E-13	0
ETHANOL	0,0632243	0,0294165	0,0101578	0,000173694	0,00121816
S-SUCCIN	0,000367193	0,000327525	0,000345587	0,1005809	7,67E-05
RHAMNOSE	1,53E-05	1,35E-05	1,35E-05	0,0105991	2,76E-06
GALAACID	1,10E-06	5,79E-07	2,75E-07	0,0766099	2,25E-08
GLUCACID	5,17E-07	2,72E-07	1,29E-07	0,0360517	1,06E-08
OXO	0,000443121	0,000379918	0,00036477	0,0799887	6,87E-05
FUCOSE	5,98E-05	5,71E-05	6,44E-05	0,00507778	1,49E-05
Total Flow kmol/hr	726,5895	488,4296	279,7369	11,98863	53,94882
Total Flow kg/hr	13096,36	8805,042	5045,724	561,0117	973,7794

B

Appendix 2

Table B.1: Solubility data for the different compounds.

Compounds	*Moleculeformula*	*Solubility*	*Comment*
Fucose	C6H12O5		
Arabinose	C5H10O5		
Rhamnose	C6H12O5		
Galactos	C6H12O6		
Glucose	C6H12O6	1200g/L (at 30C)	
Xylose	C5H10O5		
Mannose	C6H12O6		
Galacturonic acid	C6H10O7		
Glucuronic acid	C6H10O7		

Table B.2: Solubility data for the different compounds.

Compounds	*Moleculeformula*	*Solubility*	*Comment*
Butyric acid	C3H7COOH	60g/L (at 25C)	
Succinic acid	(CH2)2(COOH)2	83,2g/L (at25C)	
Acetic acid	CH3COOH	1000g/L (at 25C)	miscible
Lactic acid	CH3CH(OH)COOH	1000g/L	miscible
Carbondioxid	CO2	2,9g/L (at 25C)	
Lysine	C6H14N2O2	1000g/L (at20C)	miscible
Ethanol	C2H5OH	1000g/L (at 25C)	miscible
Glycerol	C3H8O3	5296g/L (at25C)	miscible
Acetate	CH3COO-		
2-oxoglutaric acid	C5H6O5		
Adipic acid	(CH2)4(COOH)2	2.32 wt% at 25C	1.122 wt% at 10C
Ammonia	NH3	482g/L (at 24C)	
Alanine	C3H7NO2	165g/L (at25C)	
Glycine	C2H5NO2	249g/L (at25C)	
Dihydroxyacetone	C3H6O3	930g/L at 25 C	
Glycerol	C3H8O3	5296g/L (at25C)	
Trehalose	C12H22O11	87,3g/100water (20C)	73,4g/100g water (10C)
Acetate	CH3COO-	1000g/L (at 25C)	miscible
Pyruvate	CH3COCOO-	1000g/L (at 20C)	
Lactate	CH3CH(OH)COO-	1000g/L	miscible