

# Process simulation of HMF production from wheat bran and sugar beet pulp

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# Preface

This thesis has not been the work of one person, and I would therefore like to thank the people who have helped me throughout the process of both writing my master thesis and throughout my journey to becoming a chemical engineer. Firstly, I would like to thank my supervisor, senior lecturer Mats Galbe, who has always been eager to help whenever I needed guidance, not only during my thesis but also during other courses throughout my master. I would also like to thank my examiner, professor Ola Wallberg, whose joy for chemical engineering has really inspired me. I would like to thank my friends and fellow classmates during my engineering education, this has been the five most fruitful years of my life thus far and it would not have been as fun without you.

A special thanks goes out to my long-time friends Awang, Bam and Matilda, for always making me laugh even though we do not see each other as often as I would like to, and to my very best friend Vilma, who is always there for me no matter what.

This thesis would not have been possible without the support from my family, my mom Marie, dad Anders, and sister Klara. You mean everything to me.

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Matilda Petersson, Lund, August 2021



# Abstract

Due to the progressing environmental problems related to global warming, the chemical industry is transitioning from fossil to renewable feedstocks. For added environmental benefits, surplus biomass from the agricultural industry which currently does not have any high-value applications can be used for production of chemicals. This master thesis is written as a part of the techno-economic analysis in the Farm2furan research project at Lund University, in which surplus agricultural biomass streams in Sweden are used for production of 5-hydroxymethylfurfural (HMF) in a future biorefinery. HMF is a platform chemical, and chemicals produced from HMF can be used for production of monomers, resins, textile dyes, pharmaceuticals, flavors, and fragrances.

In this thesis, the simulation software Aspen Plus was used to build a model for production of HMF from wheat bran and sugar beet pulp. To assess how the system behaved a simplified model was built initially, after which a more advanced model including all unit operations needed was built. The simulations showed that the wheat bran- and sugar beet pulp-based processes were favored by different combinations of pretreatment steps, which also greatly affected the amount of physical equipment needed. This depends on the composition of the raw material itself and the accessibility of the monosaccharides in the raw material, which ultimately affects the economic viability of the simulated processes. For wheat bran, the maximum yield of HMF from the entirety of the raw material was 19.4%, while the theoretical yield was 29.8%. For sugar beet pulp, the maximum yield was 5.6% while the theoretical yield was 17.7%. Even though both processes showed potential for profitability at this early stage of the process design, the wheat bran process consistently had greater potential with the used indicator. Because of the assumptions made in the process simulation, it is recommended that a more thorough process simulation is made including reaction kinetics before moving on to a potential pilot plant.

# Sammanfattning

På grund av de ökade miljörelaterade problemen kopplade till den globala uppvärmningen så går den kemiska industrin över från fossila till förnybara råmaterial. Överbliven biomassa från jordbruket med lågt värde kan användas för att producera kemikalier för att på så sätt uppnå en ökad miljömässig vinning. Denna masteruppsats skrivs som en del av den tekno-ekonomiska analysen inom forskningsprojektet Farm2furan vid Lunds universitet. I Farm2furan-projektet används överskottsbiomassa från det svenska jordbruket för produktion av 5-hydroximetylfurfural (HMF) i ett framtida bioraffinaderi. HMF är en plattformskemikalie som kan användas för att producera kemikalier som kan användas som monomerer, ytbeläggningar, textulfärger, läkemedel, smakämnen och doftämnen.

I denna uppsats används simuleringsprogramvaran Aspen Plus för att bygga en modell för produktion av HMF från vetekli och sockerbetsmassa. För att utvärdera hur systemet betedde sig gjordes först en förenklad modell, vilken senare komplicerades till en komplett modell som innehöll alla enhetsoperationer som behövdes. Simuleringarna visade att de vetekli- och sockerbetsmassa-baserade processerna gynnades av olika kombinationer av förbehandlingssteg, vilket också påverkade mängden utrustning som behövdes i systemet. Detta beror på sammansättningen i råmaterialet samt hur tillgängliga monosackariderna är i råmaterialet, vilket i sin tur påverkar den ekonomiska lönsamheten hos de simulerade processerna. Det maximala utbytet av HMF från hela fraktionen av råmaterial var för vetekli 19.4% och för sockerbetsmassa 5.6%. De jämförbara teoretiska utbytena var för vetekli 29.8% och för sockerbetsmassa 17.7%. Båda processerna visade potential för lönsamhet på detta tidiga stadium av processdesignen, men vetekliprocessen visade genomgående större potential för lönsamhet enligt den använda indikatorn. På grund av antagandena som gjordes i processsimuleringen rekommenderas det att en grundligare processsimulering görs, där bland annat reaktionskinetik bör ingå, innan en eventuell pilotanläggning för processerna görs.

# Table of Contents

<b>1</b>	<b>Introduction .....</b>	<b>1</b>
1.1	Project description .....	1
1.2	Aim and question formulation .....	1
1.3	Scope.....	1
1.4	Disposition .....	2
<b>2</b>	<b>Background .....</b>	<b>3</b>
2.1	Furans – applications and properties.....	3
2.1.1	Furans .....	3
2.1.2	5-hydroxymethylfurfural .....	3
2.2	Raw material .....	4
2.2.1	Wheat bran and sugar beet pulp.....	4
2.2.2	Extraction of sugar from raw material.....	5
2.2.3	Similar products to HMF produced from sugar.....	8
2.3	Conversion of sugar to HMF and separation of by-products.....	9
2.3.1	Steps to convert sugar to HMF .....	9
2.3.2	By-products and separation strategy.....	11
2.4	Block flow diagram.....	14
2.4.1	Pretreatment.....	14
2.4.2	Separation .....	15
2.4.3	Catalytic isomerization .....	15
2.4.4	Catalytic dehydration.....	15
2.4.5	Separation .....	15
2.4.6	Recirculation.....	16
2.5	Aspen Plus .....	16
<b>3</b>	<b>Process simulation .....</b>	<b>17</b>
3.1	Process simulation using simpler blocks .....	17
3.1.1	Simplified simulation of wheat bran to HMF.....	17
3.1.2	Simplified simulation of sugar beet pulp to HMF .....	22
3.2	Process simulation using advanced blocks .....	27
3.2.1	Reactors .....	27
3.2.2	Separation and recirculation .....	48
3.2.3	Heat recovery system, utilities, and pressure changers .....	62
<b>4</b>	<b>Economic evaluation.....</b>	<b>73</b>

<b>5</b>	<b>Results and discussion.....</b>	<b>77</b>
5.1	Results of the process simulation .....	77
5.2	Discussion.....	84
<b>6</b>	<b>Conclusions .....</b>	<b>89</b>
<b>7</b>	<b>References .....</b>	<b>90</b>
<b>Appendix</b>	<b>.....</b>	<b>i</b>
	Appendix A. Calculations made for the simple blocks process simulation .....	i
	A.1 Wheat bran .....	i
	A.2 Sugar beet pulp.....	ii
	Appendix B. Additional process simulation inputs in the advanced blocks simulation .....	iv
	B.1 Wheat bran.....	iv
	B.2 Sugar beet pulp .....	viii
	Appendix C. Calculations made for the advanced blocks reactor simulation – wheat bran ....	
	.....	xv
	Appendix D. Calculations made for the advanced blocks reactor simulation – sugar beet pulp	
	.....	xxi
	Appendix E. Comparison of the reactor combinations simulated with advanced blocks .....	
	.....	xxvi
	Appendix F. Calculations made for the advanced blocks separation and recycling system simulation – wheat bran .....	xxvii
	Appendix G. Calculations made for the advanced blocks separation and recycling system simulation – sugar beet pulp .....	xxviii
	Appendix H. Calculations of the theoretical yield of HMF from wheat bran and sugar beet pulp .....	xxx
	Appendix I. Calculations of the yield of HMF from wheat bran and sugar beet pulp obtained in the process simulations .....	xxxii



# 1 Introduction

## 1.1 Project description

The world faces great challenges connected to global warming and considerable changes need to be made in the coming years. In Sweden, the industrial sector stands for about a third of the total CO<sub>2</sub> emissions during 2019, and the chemical industries and oil refineries stand for 9% and 14% of the industrial emissions respectively<sup>1</sup>. To lower the emissions, it is important for the industries to change from fossil to renewable feedstocks and thus become more environmentally friendly. A part of the solution is to produce valuable chemicals from surplus biomass from the agricultural industry in biorefineries. In the Farm2furan project surplus biomass, such as wheat bran and sugar beet pulp, is used for production of hydroxymethylfurfural, shortened HMF.<sup>2</sup> In this thesis, an Aspen Plus model is made to simulate production of HMF from wheat bran and sugar beet pulp. This thesis is a part of the techno-economic analysis of the Farm2Furan project.

## 1.2 Aim and question formulation

The aim of this thesis is to build an Aspen Plus model for production of hydroxymethylfurfural from wheat bran and sugar beet pulp. HMF is a platform chemical that plays an important role in future biorefineries, as it can be used for production of chemicals for polymers and resins. In addition, the aim of the thesis is to answer the following questions: What are furans used for and why is production of furans relevant? How can sugar be extracted from wheat bran or sugar beet pulp? Are there any products similar to HMF that can be produced from the sugar? What steps are needed to convert sugar to HMF? What combination of steps has shown to be most effective regarding selectivity and yield? What by-products are formed in the process? What is needed to produce a model that simulates production of HMF from wheat bran and sugar beet pulp in Aspen Plus? Which assumptions need to be made? How does the model perform economically?

## 1.3 Scope

Two process simulation models with different complexities will be made for the two raw materials, all of which in Aspen Plus. The first model with more simple blocks will be made to get a perception of how the system behaves, after which the second model will be made with a complete process design, including separation units, heat exchangers etc. Neither of the Aspen Plus models will include reaction kinetics, as reliable kinetical data can be hard to find for the specific reactions. Implementation of reaction kinetics also adds complexity to the process simulation. The thesis will only include a basic economic comparison of purchasing prices of the raw material and reactants compared to the selling price of the product.

## **1.4 Disposition**

The disposition of the thesis is as follows: In section 2, the theoretical background of the thesis is thoroughly investigated. In section 3, the method of the process simulation is described for both the simple blocks and complex blocks. In section 4, the economic viability of the process is evaluated using an indicator called Metric for Inspecting Sales and Reactants. In section 5, the results of the process simulation are presented and discussed. In section 6, the conclusions drawn from the thesis are presented, and in section 7 the references can be found. Lastly, appendices with additional information are included in the thesis.

## 2 Background

### 2.1 Furans – applications and properties

#### 2.1.1 Furans

Furans are a class of organic heterocyclic compounds containing four carbon atoms and an oxygen atom<sup>3</sup>. The simplest compound in the class is called furan and consists of a single heterocyclic ring<sup>4</sup>. The furan ring is aromatic; however, it is less aromatic than other common heterocyclic compounds<sup>5</sup>. Furans are formed when carbohydrates are dehydrated, which happens naturally when food is heated<sup>3</sup>. Furans are used in a variety of different applications, for example as chemical intermediates, chemical feedstocks for production of resins and polymers and as solvents<sup>5</sup>.

#### 2.1.2 5-hydroxymethylfurfural

5-hydroxymethylfurfural is a compound which consists of a furan ring connected to both alcohol and aldehyde functional groups. Its preferred IUPAC name is 5-(hydroxymethyl)furan-2-carbaldehyde<sup>6</sup>. HMF is formed by dehydration of monosaccharides and can also form naturally during heating of foods<sup>7, 8</sup>. The molecular formula is  $C_6H_6O_3$ , it has a molecular weight of 126.11 g/mol, a melting point of 28-34°C and a boiling point of 114-116°C at 1 hPa. HMF is freely soluble in water, methanol, ethanol, acetone, ethyl acetate and dimethylformamide.<sup>3</sup> HMF is a thermally unstable molecule which decomposes at high temperatures. Notable rehydration and condensation has been reported at 130°C.<sup>7-9</sup> Most producers sell HMF with a purity of 99%, and the price varies from as little as \$5/kg to \$600/kg, with an average price at \$240/kg<sup>10</sup>. Bozell and Petersen suggest HMF as one of the important biorefinery platform molecules that can be produced from carbohydrates in an article from 2010 where the US Department of Energy's top 10 suggested important biorefinery platform molecules were revisited<sup>11</sup>. HMF has the potential to act as a replacement platform chemical for products that are currently produced from fossil resources<sup>12</sup>. Because of its structure with primary hydroxyl and formyl groups, HMF can be converted to other compounds with interesting properties<sup>7</sup>. These compounds can be used in an array of different applications, for example as monomers, in pharmaceuticals and as flavours and fragrances. Two molecules that have been mentioned as particularly interesting are 2,5-furandicarboxylic acid (FDCA) and levulinic acid.<sup>3</sup> Levulinic acid is a specialty chemical used as a component in a variety of different applications, ranging from polymer resins to textile dyes<sup>13</sup>. FDCA has been reported as a substitute for terephthalic acid in polyester production<sup>11</sup>.

## 2.2 Raw material

### 2.2.1 Wheat bran and sugar beet pulp

Today, there are several by-products from the agricultural industry that can be used as feed-stocks in future biorefineries<sup>2</sup>. Wheat bran, a by-product of the milling industry, is separated from the wheat grain during production of wheat flour<sup>12</sup>. Wheat bran consists of three main constituents: residual starch, hemicellulose and cellulose<sup>14</sup>. 150 million tons of wheat bran would be produced per year if assumed that all wheat for human consumption was milled. Today, the main use of wheat bran is in animal feed and a smaller part is consumed by humans.<sup>15</sup> As the products in these applications are of low value, there is an interest to obtain valuables from wheat bran to produce chemicals such as HMF<sup>12</sup>.

Every year, roughly 270 million tons of sugar beets are produced. The remainder of the sugar beet after the extraction of sucrose is called sugar beet pulp. Today, the main use of sugar beet pulp is in animal feed, which is produced from sugar beet pulp in a costly process.<sup>16</sup> The main constituents in sugar beet pulp are cellulose and pectin<sup>17</sup>. Wet sugar beet pulp normally contains 6-12% dry matter, pressed sugar beet pulp contains 18-30% dry matter and dried sugar beet pulp contains 87-92% dry matter<sup>18</sup>.

More detailed, general compositions of wheat bran and sugar beet pulp can be seen in Table 1 and Table 2 respectively.

Table 1. General composition of wheat bran<sup>12</sup>.

Compound	Amount [%]
Water	12.1
Protein	13.2-18.4
Fat	3.5-3.9
Total carbohydrates	56.8
<i>Starch</i>	13.8-24.9
<i>Cellulose</i>	11.0
<i>Total arabinoxylans</i>	10.9-26.0
<i>Total <math>\beta</math>-glucan</i>	2.1-2.5
Phenolic acids	1.1
Ash	3.4-8.1

Table 2. General composition of sugar beet pulp<sup>19</sup>.

Component	Percentage (% , dry basis)
Glucan	22.70
Xylan	5.14
Galactan	5.92
Arabinan	23.73
Mannan	1.85
Pectin	22.84
Acid insoluble lignin	1.04
Acid soluble lignin	0.12
Crude protein	11.42
Ash	2.51
Others	2.73

### 2.2.2 Extraction of sugar from raw material

To produce HMF, monosaccharides must be extracted from the raw material as monosaccharides are not present freely in the material<sup>17,20</sup>. This can be performed by several different methods, as described in the following parts of the report. The reaction path to produce HMF is via fructose, but recent studies say that HMF also can be produced from glucose. The glucose then isomerizes to fructose, and dehydration takes place.<sup>3,7</sup> Production from glucose is favourable from a biomaterial standpoint, as glucose is more abundant in the raw materials as it is the monosaccharide, among other constituents, that builds up hemicellulose and cellulose, which are more abundant in the raw materials<sup>12,19</sup>. Therefore, the focus in the following parts has been to identify how glucose and glucose-like monosaccharides can be extracted from wheat bran and sugar beet pulp via different methods. Generally, there is not a single extraction method that is universally best for all raw materials. The effectiveness of the extraction method is highly dependent on a number of different factors, including which raw material is used.<sup>20</sup>

#### 2.2.2.1 Steam explosion

Steam explosion is a pretreatment method for biomass in which the biomass is treated with high-pressure saturated steam. Then, the pressure is quickly released, and the water-soluble components are released as the biomass undergoes explosive decompression.<sup>17</sup> Steam explosion is normally performed at pressures between 1-3.5 MPa and temperatures between 180-240°C<sup>21</sup>. Cárdenas-Fernández et al. used steam explosion to pretreat sugar beet pulp to separate the water-insoluble cellulose from the water-soluble pectin. By subjecting the sugar beet pulp to varying times and pressures, the authors found a predicted optimum at 5.3 bar and 24.4 min. This yielded 83.2% solubilized arabinose and 4.8% solubilized glucose. The maximum solubilized glucose was found to be 10% at 8 bar and 30 min.<sup>17</sup>

### 2.2.2.2 *Enzymatic hydrolysis*

Enzymatic hydrolysis can be used to release the individual monosaccharides from polysaccharides such as pectin, cellulose, and hemicellulose. Different enzymes are used depending on the desired targeted monosaccharide. In an article by Cárdenas-Fernández et al.<sup>17</sup>, enzymatic hydrolysis was performed to separate L-arabinose from the water-soluble fraction obtained by steam explosion of sugar beet pulp. The experiment yielded release of 87% of the arabinose after incubation for 8 hours using 100 mg of L-arabinofuranosidase per ml of substrate at pH 7 and 60°C. The water-insoluble fraction was treated with cellulase to release glucose. Incubation of 0.5 mg of cellulase per g of solid at 50°C for 24 hours yielded 19 g/l of soluble glucose. In Zheng et al.<sup>19</sup>, sugar beet pulp was first pretreated with dilute acid to solubilize hemicellulose and increase the enzymatic degradability of cellulose. Then, enzymatic hydrolysis was performed for 72 h at 50°C with 2% (w/w) solid concentration at pH 4.8. This resulted in a maximal total reducing sugar of 62 wt.% (dry matter) including both dilute acid pretreatment and enzymatic hydrolysis. Alexandri et al.<sup>16</sup> treated sugar beet pulp with enzymes to hydrolyse cellulose after treating with dilute acid, as described in section 2.2.2.3. The highest concentrations of glucose were achieved by first treating with acid for 15 min at 10% (w/v) initial solids and 30 min at 10% (w/v) initial solids respectively and then using 0.1 ml of Accelerase 1500 per g of cellulose. This resulted in  $8.89 \pm 0.03$  g/l and  $9.62 \pm 0.03$  g/l of glucose released respectively. According to Chotěborská et al.<sup>14</sup>, pure enzymatic hydrolysis is not sufficient to achieve high yields of pentoses and hexoses from wheat bran. The process was instead divided into two steps, where the first involved hydrolyzation of the starch using amylases. This resulted in 38 g D-glucose/100 g dry matter. The second step involves acidic hydrolysis and will be described in section 2.2.2.3. Jiang and Guo<sup>22</sup> concluded that steam explosion is a useful pretreatment method for enzymatic hydrolysis of wheat bran. Firstly, the wheat bran was pretreated by steam explosion at 1 MPa and 200°C for 120 seconds. Then, 3% (w/w) of cellulase and xylanase respectively were used at 50°C for 48h at pH 5.2 and continuous agitation at 120 rpm. This resulted in the maximal obtained concentration of reducing sugars, 194.6 mg per g of dry wheat bran, as well as the highest concentration of glucose, 120.4 mg/g. Without using steam explosion as a pretreatment, the same conditions yielded 119.4 mg/g of reducing sugars. Palmarola-Adrados et al.<sup>23</sup> investigated a variation of different extraction methods on the starch-free bran fraction of wheat bran obtained by subsequent liquification and saccharification to remove the starchy fraction. It was concluded that pretreatment with 0.2% H<sub>2</sub>SO<sub>4</sub> at 160°C for 20 minutes with enzymatic hydrolysis gave the highest yield of total sugar of 53.0 g/100 g starch-free bran, of which 16.4 g/100 g was glucose. The highest yield of glucose, 17.7 g/100 g starch-free bran, was obtained by pretreatment without acid at 170°C for 20 minutes followed by enzymatic hydrolysis.

### 2.2.2.3 *Acid hydrolysis*

Acid hydrolysis is often used as an alternative to enzymatic hydrolysis. In an article by Cárdenas-Fernández et al.<sup>17</sup>, the water-soluble fraction obtained by steam explosion treatment of sugar beet pulp was subjected to acidic hydrolysis. The water-soluble pectin fraction was treated with 2.5% (v/v) H<sub>2</sub>SO<sub>4</sub> for 1 hour at 121°C and then adjusted to pH 6 using NaOH. The treatment resulted in a concentration of 20 g/l of total sugars in the hydrolysed material. Alexandri et al.<sup>16</sup> hydrolysed hemicellulose in sugar beet pulp by treatment with H<sub>2</sub>SO<sub>4</sub> and HCl, respectively, to hydrolyse hemicellulose. H<sub>2</sub>SO<sub>4</sub> was found to be favourable because of less formation of inhibitors for the microorganisms used in the subsequent fermentation. The highest yields of glucose and fructose were achieved when pretreating at 121°C for 15 min and 30 min respectively, both using 15% (w/v) solid loading.

Treatment for 15 min resulted in concentrations of  $7.35 \pm 0.88$  g/l of glucose and  $7.75 \pm 1.69$  g/l of fructose. Treatment for 30 min resulted in concentrations of  $6.11 \pm 0.87$  g/l of glucose and  $5.36 \pm 1.69$  g/l of fructose. After the pretreatment, enzymatic hydrolysis was performed, as described in the corresponding part of the report. In the second treatment step described in Chotěborská et al.<sup>14</sup>, starch free residue from wheat bran was treated with H<sub>2</sub>SO<sub>4</sub> at high temperatures to release pentoses and hexoses. The maximum concentration of D-glucose, 7.5 g per 100 g starch free residue, was achieved at 170°C for 30 minutes using 2% H<sub>2</sub>SO<sub>4</sub> per weight of slurry.

#### 2.2.2.4 *Hydrotropic extraction*

Hydrotropes can be used for fractionation of biomass<sup>24</sup>. They are characterized by the capability to increase solubility of organic molecules in water that otherwise are not normally soluble to the same extent. Hydrotropes have an amphiphilic structure and contain both a hydrophilic and hydrophobic region. Common hydrotropic molecules include sodium benzoate, sodium 1,3-benzenedisulfonate and sodium benzene sulfonate.<sup>25</sup>

#### 2.2.2.5 *Deep eutectic solvents*

Deep eutectic solvents can be used for fractionation of biomass<sup>24</sup>, and are defined as mixtures of two or more compounds that have a melting point lower than the compounds individually. Deep eutectic solvents are made by mixing a hydrogen bond acceptor with a hydrogen bond donor. Hydrogen bond acceptors can be e.g., quaternary ammonium or phosphonium salt, and hydrogen bond donors can be e.g. acids, alcohols or amines.<sup>26</sup>

#### 2.2.2.6 *NaOH treatment*

Mense and Shi<sup>27</sup> describe how destarched and deproteinized wheat bran undergoes treatment with sodium hydroxide and urea for solubilization of the material. The authors report that 80% of the bran was dissolved in the experiment. Thuvander<sup>28</sup> also used NaOH to extract hemicellulose from wheat bran prior to membrane filtration, which is described in section 2.2.2.7.

#### 2.2.2.7 *Membrane filtration*

A way to concentrate and purify hemicellulose is to use membrane filtration. Thuvander<sup>28</sup> used membrane filtration to recover hemicelluloses from wheat bran. Firstly, the bran was destarched. NaOH is then used to extract the hemicelluloses from the starch-free bran, after which the solids are removed to leave only arabinoxylan, which is the targeted fraction. A combination of ultrafiltration, diafiltration and nanofiltration is then used to recover the remainder of the NaOH and to purify the arabinoxylan.

#### 2.2.2.8 *Extraction of starch with water*

Sardari et al.<sup>29</sup> suggest extraction methods to perform subsequent extraction of starch, lipids, and proteins from wheat bran without using harsh treatments that may disrupt the other fractions. Starch was extracted from 10 g samples of wheat bran of two different particle sizes using 100 ml of tap water at 30°C. The samples were placed in a baffled shake flask and incubated in a shaker incubator at either 30°C for 30 min or 55°C for 4 h. The highest yields were obtained for the coarse bran, where  $81.7 \pm 0.67\%$  of the starch was isolated when treated at 55°C for 4 h, but the extraction at 55°C was found to be less favourable from a separation standpoint due to higher solubilization in water.  $67.7 \pm 1.9\%$  of the starch was extracted in coarse bran when treated at 30°C for 30 min.

#### 2.2.2.9 *Combinations of extraction methods*

Zheng et. al.<sup>19</sup> concludes that dilute acid pretreatment improves the enzymatic hydrolysis of sugar beet pulp. Alexandri et al.<sup>16</sup> also performs acid pretreatment on sugar beet pulp before performing enzymatic hydrolysis with good results. Jiang and Guo<sup>22</sup> concluded that steam explosion is a useful pretreatment method for enzymatic hydrolysis of wheat bran. A clear improvement between performing pretreatment or not could be seen on the obtained concentration of reducing sugars. Palmarola-Adrados et al.<sup>23</sup> concludes that acidic pretreatment on wheat bran is favourable for enzymatic hydrolysis, but also that pretreatment using heat before enzymatic hydrolysis can be favourable for glucose extraction.

#### 2.2.3 **Similar products to HMF produced from sugar**

Two similar products to HMF that also can be produced from sugar are the organic acids succinic acid and levulinic acid. Both chemicals were mentioned in the 2010 article by Bozell and Petersen in which the US Department of Energy's top 10 suggested important biorefinery platform molecules were revisited. Succinic acid is produced by fermentation of glucose.<sup>11, 30</sup> It can be used as a platform chemical to produce other chemicals that have applications in e.g., pesticides, dyes and in pharmaceutical applications<sup>31</sup>.

Levulinic acid is produced from HMF by readdition of water to split the furan ring, which produces levulinic acid and formic acid. Levulinic acid, like HMF and succinic acid, is a platform chemical that can be used to produce other chemicals.<sup>11</sup> It can be used for production of chemicals with applications in pharmaceuticals and in plasticizers<sup>32</sup>.

## 2.3 Conversion of sugar to HMF and separation of by-products

### 2.3.1 Steps to convert sugar to HMF

To convert sugar extracted from biomass into HMF in an efficient way, all the facts regarding performed research on the subject must be considered. One of the more important outcomes is that fructose dehydrates to HMF faster than does glucose while also resulting in higher yields. Despite this, glucose is more abundant in biomass than fructose. To deal with these aspects, the following process steps for conversion of glucose to HMF have been identified: isomerization of glucose to fructose and dehydration of fructose to HMF.<sup>3, 7, 33</sup>

#### 2.3.1.1 Isomerization of glucose to fructose

Commercially, the isomerization is performed by employing an enzyme, glucose isomerase, resulting in an equilibrium mixture of glucose and fructose. Just as any enzyme, D-xylose isomerase, also called glucose isomerase, requires specific conditions to function properly. Fructose is more expensive than glucose because of the use of enzymes for the commercial production.<sup>34, 35</sup> Tomasiak and Horton<sup>36</sup> report that 55% fructose solution can be obtained from starch by employing glucose isomerase at a temperature of 110°C. The commercial equilibrium reaction takes place at 45°C and yields a fructose concentration of 48%. By using a chemical catalyst the isomerization reaction proceeds faster.<sup>33</sup> When using glucose isomerase from Novozymes, 1 kg liquid produces over 18 ton of 42% fructose solution<sup>37</sup>. Even if a chemical catalyst is used, the isomerization step is still the rate-determining step when producing HMF from glucose via fructose, which makes finding an optimal catalyst of great importance for HMF production<sup>38</sup>.

Motagamwala et al.<sup>8</sup> report that the minimum selling price of the process for production of HMF from fructose using a solvent system of acetone and water is mostly dependent on the feedstock cost. Because of the low price and abundance of glucose, efforts are made to use it as a feedstock in the process. The conversion of glucose to HMF takes place in two steps: firstly, the glucose isomerizes to fructose over a Lewis acid catalyst and secondly, the fructose is dehydrated to form HMF. Motagamwala et al. use Sn- $\beta$ , a heterogeneous acid catalyst, to isomerize glucose to fructose. Using the catalyst combined with a solvent system of 80/20 acetone/water at 353 K, the result was an equilibrium mixture of glucose, fructose, and mannose. The step involving dehydration of fructose to HMF is described in section 2.3.1.2.

Oozeerally et al. studied the use of Y zeolites prepared with gallium and tin for isomerization of glucose into fructose and mannose, as well as conversion of glucose to HMF. After preparation of the catalyst, 40 mg of catalyst was placed in a reactor for 3 h at 140°C together with glucose solution and the chosen solvent, DMSO. The use of DMSO on the catalyst system when performing direct conversion of glucose resulted in higher selectivities towards HMF. However, DMSO is an undesirable solvent industrially because of its environmental impact. The most active catalyst for isomerization of glucose was Sn-deAl-HY, tin-containing Y zeolite. It is stated that Sn- $\beta$  is the most commonly used catalyst for glucose isomerization, with 54% conversion of glucose and 30% and 9% yield to fructose and mannose respectively when subjected to similar conditions as the ones used in Oozeerally et al.<sup>38, 39</sup>

### 2.3.1.2 Dehydration of fructose to HMF

Generally, HMF synthesis from carbohydrates can be divided into three types of processes, traditional single-phase systems, biphasic systems, and ionic liquid-based systems. In addition, the solvents used can be aqueous, non-aqueous or mixed.<sup>3</sup> Both homogeneous and heterogeneous acid catalysts can be used for all the systems and solvents. Alkaline catalysts have been shown to inhibit the formation of HMF and are therefore not used. In total, three water molecules are removed from fructose to yield HMF.<sup>3, 40</sup>

van Putten et al.<sup>3</sup> compile results from a collection of different experiments involving dehydration of fructose using different catalysts and solvents. The highest yield of HMF in an aqueous system without catalyst was 56 mol% when using 4.5 wt.% fructose, allowing the reaction to proceed for 1.5 h at 175°C. For homogeneous catalysts in aqueous systems, 9 wt.% fructose, PEG as cosolvent and 200 mol% HCl as catalyst at 95°C for 1.5 h resulted in the highest yield of HMF, 68 mol%. The obtained conversion and selectivity were 86 mol% and 79 mol% respectively. The highest yield of HMF in aqueous systems using a heterogeneous catalyst was 73 mol%, achieved by reacting 2 wt.% fructose, 70 wt.% acetone as cosolvent and 100 wt.% Dowex 50wx8-100 as catalyst at 150°C for 15 min. The corresponding conversion and selectivity were 90 mol% and 81 mol% respectively. In general, it is seen that use of catalysts for dehydration of fructose results in higher yields of HMF for aqueous systems. Higher fructose concentrations coincide with polymerization reactions, which lowers the yield of HMF. Trends in homogeneous and heterogeneous systems are hard to identify because of the variation in results, which makes comparison of the two difficult. To increase the selectivity for HMF at higher conversions, stabilization may have to be included to prevent rehydration of HMF to levulinic acid and formic acid.

Research on dehydration of fructose using non-aqueous solvents is predominantly performed using DMSO as solvent. One study reported an obtained yield of HMF of 72 mol% when employing DMSO as solvent, 8 wt.% fructose and letting the reaction proceed for 4 h at 130°C, with 100 mol% conversion and 72 mol% selectivity.

For homogeneous catalysts in organic solvents, some of the highest yields were achieved by the combination of DMSO as solvent and ionic liquids as catalyst. With 3 wt.% fructose solution, 50 or 200 mol% catalyst at 100 or 160°C for 4 min, yields of 88-93 mol% were achieved. The corresponding conversion and selectivities were 100 mol% and 88-93 mol%, respectively.<sup>3</sup> When employing heterogeneous catalysts in combination with organic solvents, many studies utilize continuous water removal. Yields, conversions and selectivities of 100 mol% have been achieved with DMSO as solvent and 6 wt.% Amberlyst 15 powder as catalyst at fructose concentrations of 3 and 50 wt.%, respectively when letting the reaction proceed for 2 h at 120°C. Yields of 97 mol% were achieved at 3 wt.% fructose and the same conditions as previously mentioned when employing catalysts FePW<sub>12</sub>O<sub>40</sub> and H-BEA zeolite respectively.<sup>3, 41</sup> van Putten et al. report that overall, the selectivity and yield of HMF in organic solvents are higher than in aqueous systems. Lower temperatures can be used, which is seen as an advantage. The problem with using DMSO as the solvent is that it is difficult to separate from HMF and major amounts of extraction chemicals may be needed, which demands high amounts of energy. DMSO is also reported to be unstable above 100°C, which is the temperature used for all of the mentioned experiments in this section.<sup>3</sup>

When biphasic systems are used for fructose dehydration, the reaction occurs in an aqueous solvent with subsequent extraction in an organic solvent, to prevent undesired conversion to by-products. An HMF yield of 85 mol% was obtained in a system of 1:1 water/DMSO (w/w) and 7:3 MIBK/2-butanol (w/w) as extraction solvent using HCl as catalyst. A yield of 90 mol% was achieved in a biphasic system with water and 2-butanol as the two phases and TA-p as catalyst. This system also had a higher selectivity for HMF, 96 mol%, compared with 89 mol% for the system with HCl as catalyst. It can be seen that application of biphasic systems results in higher yields of HMF than aqueous systems.<sup>3</sup>

Sayed et al.<sup>40</sup> use a biphasic system composed of water and dimethyl carbonate, DMC, in a 3:1 (v/v) ratio for HMF production. HCl was chosen as catalyst to avoid humins clogging the reactor, which might be the case when employing a heterogeneous catalyst under continuous operation. Reacting a 30% (w/v) fructose and water solution with DMC and 0.23 M HCl as catalyst in a tube reactor with 1 min residence time at 200°C resulted in 96.5% fructose conversion, 87.2% yield of HMF and 90.4% selectivity. DMC proved to be a favourable solvent because of its ability to stabilize HMF, its low boiling point which makes for easier separation as well as its environmental and health sustainability.

After the catalytic isomerization reaction described in Motagamwala et al.<sup>8</sup> and in the previous part of the report, the product was subjected to a Brønsted acid catalyst to dehydrate fructose to HMF, while glucose remains unreacted. The catalyst used was Amberlyst-15. Motagamwala et al. concludes that a way to produce HMF from glucose efficiently via a two-step reaction has been found.

Pyo et al.<sup>13</sup> studies the effect of heterogeneous catalysis and different salts on the dehydration of glucose and fructose to levulinic acid, which is a chemical produced from HMF. The order of the salt anion that gave the greatest improvement of the reaction was  $\text{Cl}^- > \text{CO}_3^{2-} > \text{SO}_4^{2-}$ .

## **2.3.2 By-products and separation strategy**

### *2.3.2.1 By-products from the different parts of the process*

#### **2.3.2.1.1 By-products from extraction of sugar from the raw material**

By-products from the extraction process will include a variety of different compounds, including the components present in the raw material before extraction. These will include water, carbohydrates, hemicellulose, cellulose, pectin, lipids, proteins and acid or enzymes used for the extraction process.<sup>12, 19</sup>

#### **2.3.2.1.2 By-products from isomerization of glucose to fructose**

Unreacted glucose, mannose and humins are by-products of isomerization of glucose to fructose, as stated in Oozeerally et al. The production of humins can be minimized by using DMSO as a solvent, which also increases the yield of HMF in the following reaction step.<sup>38</sup> Rajabbeigi et al. reports the formation of lactic acid when using Sn- $\beta$  as a catalyst for glucose isomerization at 160°C<sup>34</sup>.

### 2.3.2.1.3 By-products from dehydration of fructose to HMF

van Putten et al.<sup>3</sup> report that the types of by-products formed during dehydration of hexoses is reliant on the feedstock used as well as the process conditions, but also that both quantitative and qualitative data on by-products often is not included in the studies.

The following compounds have been identified as by-products from dehydration of hexoses to HMF: 2-hydroxyacetylfruran, furfural, HMF dimers, levulinic acid, formic acid, acetic acid, 1,2,4-trihydroxybenzene, fructose dianhydride and polymeric material (including humins). As previously mentioned, the formation of some of the compounds can be prevented. Two examples are the formation of levulinic acid and formic acid, which are formed through rehydration of HMF and thus can be prevented by a non-aqueous system.

In addition to the by-products that were previously mentioned, the following by-products can be formed during reactions in aqueous systems with sub- and supercritical conditions: erythrose, pyruvaldehyde, glyceraldehyde, dihydroxyacetone, lactic acid and glycolaldehyde.<sup>3</sup>

### 2.3.2.2 Separation strategy

#### 2.3.2.2.1 Extraction

Membrane filtration can be used for separation of the components in biomass. Depending on the desired fraction, different membranes are used. As described by Krawczyk<sup>42</sup>, microfiltration have been used to remove suspended matter, ultrafiltration was used to recover hemicellulose and nanofiltration was used to obtain concentrated lignin.

Tirpanalan et al.<sup>43</sup> use nanofiltration to concentrate glucose derived from starch in wheat bran. The membrane used was an acid/base-stable flat-sheet nanofiltration membrane with a molecular weight cut off of 200 Da. Subsequent to enzymatic hydrolysis, membrane filtration resulted in a retentate with 2.7 times the concentration of glucose than that in the feed to the membrane; however, the flux through the membrane was low.

#### 2.3.2.2.2 Dehydration

Only limited research has been performed to isolate HMF from non-aqueous solvent systems; the yield of HMF is generally very high before separation has been performed. DMSO and HMF are hard to separate and large amounts of extraction chemicals are required. In addition, separation of DMSO and HMF by distillation can be complex, as DMSO is a high-boiling solvent and both compounds are less stable at higher temperatures.<sup>3, 8</sup>

It has been shown that HMF can be extracted from DMSO by using dichloromethane. Water was added to separate the two phases, which resulted in 96% of the HMF ending up in the dichloromethane phase. Subsequently, HMF was purified by crystallization.<sup>3</sup>

Zhang et al.<sup>44</sup> report successful separation of HMF from fructose, levulinic acid and formic acid, which are present in the reaction mixture after dehydration of fructose, by adsorption with hollow-structured porous polymers.

Sayed et al.<sup>40</sup> obtained HMF with purity  $\geq 93\%$  by solvent evaporation in experiments performed on a biphasic system of 3:1 water and DMC and HCl as catalyst. The two phases were separated from each other in a separation funnel.

Pawar<sup>45</sup> investigated separation of by-products such as humins, levulinic acid and formic acid from HMF by adsorption. The adsorbent used was a quaternary ammonium chloride functionalized macroporous resin, combined with isopropyl alcohol which is described as an environmentally friendly solvent. In ambient conditions, a purity of HMF above 98% was obtained.

In aqueous systems, humins can be separated from the reaction mixture obtained from dehydration of fructose by filtration or centrifugation<sup>3</sup>.

#### 2.3.2.2.3 Recirculation and purification of monosaccharide streams

Industrially, chromatography is the most common method for separation of glucose and fructose. It is widely used in the process for production of high fructose corn syrup, HCFS, in which the concentration of fructose is enriched by separation by chromatography as the equilibrium concentration is present at 42% fructose<sup>37</sup>. The method used is called simulated moving bed chromatography, SMB.<sup>46</sup> Manufacturers of different ion exchange resins used for SMB report that purities of 90% fructose can be obtained<sup>47, 48</sup>.

## 2.4 Block flow diagram

The block flow diagram has been made based on the findings from the previous sections describing the published literature on the subject and is presented in Figure 1. The proposed block flow diagram will include the following steps, which will be described in greater detail later in this section: pretreatment/extraction of sugar from sugar beet pulp or wheat bran, catalytic isomerization of glucose to fructose, catalytic dehydration of fructose to HMF and separation of by-products. Possible recirculation of streams is not included in the block flow diagram but is also discussed later in this section.

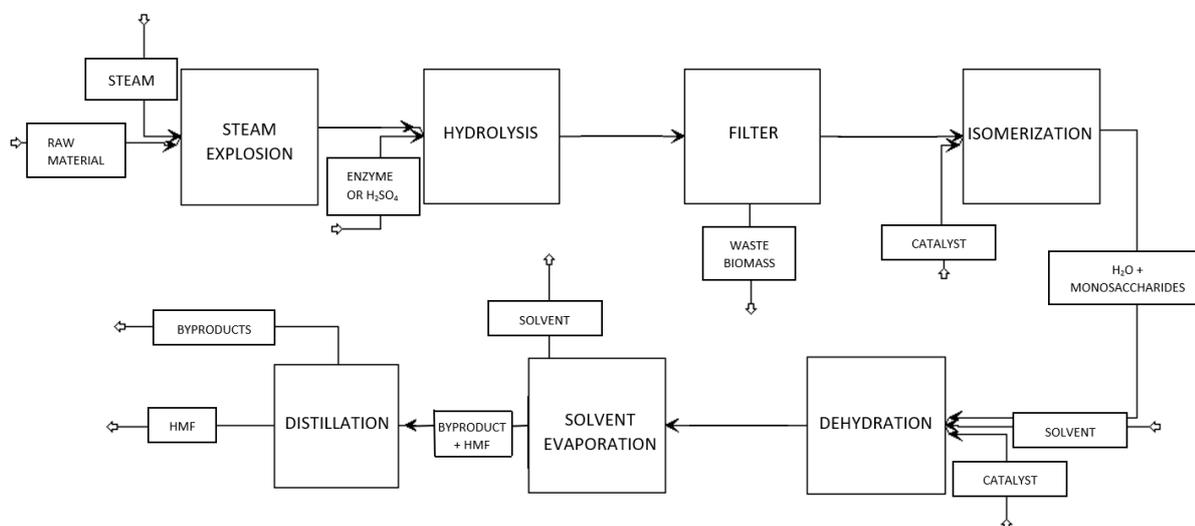


Figure 1. Block flow diagram of the process including pretreatment, isomerization, dehydration, and separation steps.

### 2.4.1 Pretreatment

Two combinations of methods are proposed for the pretreatment of wheat bran or sugar beet pulp, the first is steam explosion and acid hydrolysis and the second is steam explosion and enzymatic hydrolysis. The methods were chosen because of being extensively researched on different types of biomass, their ability to monomerize the larger molecules in the biomass to glucose as well as being possible to simulate in Aspen Plus and with accurate results. Steam explosion is performed at 180-240°C with a pressure of 1-3.5 MPa. In the literature, similar treatments resulted in 10% solubilized glucose from sugar beet pulp at 8 bar and 30 min. For wheat bran, treatment at 1 MPa for 120 s has been reported to result in 120.4 mg glucose/g dry wheat bran.<sup>17, 21, 22</sup>

The acid hydrolysis will be performed with H<sub>2</sub>SO<sub>4</sub> for both wheat bran and sugar beet pulp. 2% (w/w) will be used for wheat bran and 15% (w/v) for sugar beet pulp. Wheat bran is treated at 170°C for 30 min, which results in 7.5 g of glucose per 100 g starch free residue. The sugar beet pulp is treated at 121°C for 15 minutes, which have been shown to result in  $7.35 \pm 0.88$  g/l of glucose and  $7.75 \pm 1.69$  g/l of fructose.<sup>14, 16</sup>

For wheat bran, the enzymatic hydrolysis will be performed by using L-amyloglucosidase which is a starch-degrading enzyme, and L-endoamylase. The dosage is 1 and 1.3 l enzymes per ton of starch, respectively, and the ratio of bran and water is 1:5. After treatment at 50°C<sup>22</sup>, this reaction mixture has been reported to release 38.0 g glucose/100 g dry matter.<sup>14</sup>

For sugar beet pulp, the enzymatic hydrolysis will be performed by using 0.5 mg cellulase/g solid and incubating at 50°C for 24 h. When performed by Cárdenas-Fernández et al., the result was 19 g soluble glucose/l.<sup>17</sup>

#### 2.4.2 Separation

For separation of the by-products after the pretreatment step, membrane filtration will be used. The use of membrane filtration enables separation of the monosaccharides from the bigger molecules which might still be present after the pretreatment, while also increasing the concentration of monosaccharides the solution.<sup>42, 43</sup>

#### 2.4.3 Catalytic isomerization

Two different alternatives are suggested for the catalytic isomerization step. One is performed employing a chemical catalyst and one is performed using enzymes. The first alternative is performed by employing Sn- $\beta$  catalyst in water. 10% (w/w) glucose in water with 1:50 Sn- $\beta$ :glucose molar ratio has been reported to yield 46% glucose, 31% fructose, 9% mannose after reaction at 140°C for 12 minutes or 110°C for 30 minutes.<sup>39</sup> The other one utilizes glucose isomerase, an enzyme that converts glucose to fructose. 1 kg glucose isomerase solution produced by Novozymes results in 18 tons of 42% fructose solution<sup>37</sup>. Concentrations of 55% fructose have been reported at a temperature of 110°C<sup>36</sup>, but the equilibrium reaction takes place at 45°C and results in 48% fructose<sup>33</sup>. The method with Sn- $\beta$  catalyst in water was chosen because it is the most used chemical catalyst for the isomerization, the reaction is fast and provides a good result at a reasonable time and temperature. The enzymatic reaction using glucose isomerase was chosen due to it being the most used for the commercial process today, the enzyme being specific and the reaction resulting in a mixture of fructose and glucose, which means fewer separation steps will be needed downstream.

#### 2.4.4 Catalytic dehydration

Three different alternatives are proposed for the catalytic dehydration step. Two of them are non-aqueous systems with heterogeneous catalysts, and one is a biphasic system with homogeneous catalyst. In the first alternative, the reaction solution consists of 3 wt.% fructose, DMSO as solvent and 6 wt.% of Amberlyst 15 powder relative to the substrate. After letting the reaction proceed for 2 h at 120°C, the result is 100 mol% yield.<sup>3, 41</sup> In the second alternative, the reaction solution consists of 3 wt.% fructose, DMSO as solvent and 6 wt.% of FePW<sub>12</sub>O<sub>40</sub> relative to the substrate. After letting the reaction proceed for 2 h at 120°C, the result is 100 mol% conversion and 97 mol% yield and selectivity, respectively.<sup>3, 41</sup> The third reaction solution consists of 30% fructose in water (w/v), DMC as solvent with 3:1 water:DMC ratio and 0.23M HCl. 1 min residence time in a tube reactor at 200°C results in 87.2% yield, 96.5% conversion of fructose and 90.4% selectivity.<sup>40</sup> The three alternatives were chosen because of their high yields and selectivity of HMF. The use of organic solvents in the system has been shown to stabilize HMF, which result in less amounts of by-products.

#### 2.4.5 Separation

The final separation step will include solvent evaporation to separate the solvent from HMF. Sayed et al. reported successful separation of HMF from the organic DMC-phase in the described biphasic system when evaporating in a rotary evaporator under vacuum at 40°C, resulting in HMF with a purity of 93% and over 98% yield.<sup>40</sup> Because of the varying boiling points of HMF and the by-products produced in the dehydration reaction, separation using distillation can be possible.<sup>3, 49, 50</sup>

#### **2.4.6 Recirculation**

Recirculation of components present as catalysts, or in large amounts throughout the system, such as water or enzymes, will be performed as a last step after implementation of separation units.

Because of the equilibrium concentration between glucose and fructose being 42% fructose<sup>37</sup>, it is necessary to implement separation of the two monosaccharides to enable higher utilization rate of the sugar even if the two monosaccharides are present in the same stream after the final separation step. After separation, the glucose can be recirculated to the isomerization reactor while the fructose can be recirculated to the dehydration reactor. The separation will be performed by a chromatography column which has the ability to separate fructose and glucose to above 90% purity of fructose<sup>47, 48</sup>.

### **2.5 Aspen Plus**

Aspen Plus is a computer software program that is based on flowsheet simulations. It is one of the most used software to model chemical engineering processing plants. Aspen Plus can be used to model complete chemical processes from raw material to product by using different blocks which represent the different unit operations present in the process, as well as different streams that are used to represent the material in the process. Aspen Plus can also be used to predict the performance of a process by using engineering relationships.<sup>51</sup>

## 3 Process simulation

### 3.1 Process simulation using simpler blocks

The purpose of simulating the process with simpler blocks is to provide a starting point for the process simulation, to assess what information is needed and to understand how the system behaves. An effort is made to simulate the different alternatives for the unit operations for the two raw materials, to cover and test as much as possible which was learned from the literature study. No simulation of reaction kinetics, formation of by-products nor optimization of the heat exchanger system is made for the simple blocks processes. In addition, the concentrations of specific components to specific reactors in the process is sometimes not adjusted to be equal to those used in the literature. Throughout the processes with simple blocks, it is assumed that only cellulose and glucan react to form monosaccharides.

The simulated mass flow of raw material to the system is just 100 kg/h, which is the reason why some of the flows are very small.

All calculations performed for the simpler block simulations are found in Appendix A.

#### 3.1.1 Simplified simulation of wheat bran to HMF

The complete process flow diagram is presented in Figure 2.

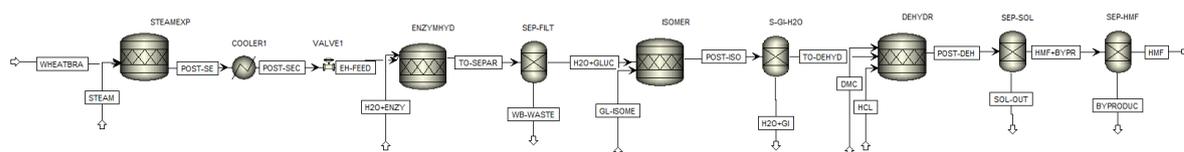


Figure 2. The complete process flow diagram for the simplified simulation with wheat bran as raw material.

The simulated composition of wheat bran proceeds from the composition stated in Table 1, with some modifications. Because of the limitations in Aspen Plus, not all the components were found and had to be replaced with comparable substances. In Table 3, all the replaced components are stated. The fat and protein fractions are replaced by the most occurrent fatty acid and amino acid respectively<sup>52, 53</sup>.

Some of the components are collected from an in-house databank used at the Department of Chemical Engineering at Lund University, which contains biobased compounds. The compounds used from the databank are cellulase, cellulose, glucose, solids (soluble solids) and xylose.

During the simulation, there were recurring warnings about missing property parameters for some of the different compounds. In that case, the missing values were taken from other similar compounds in the program “Database Manager – Aspen Properties V11”.

Table 3. Compounds and their replacements in the feed for the wheat bran simulation using simplified blocks.

Compound	Replaced with
Protein	DL-glutamic acid <sup>52</sup>
Fat	Linoleic acid <sup>53</sup>
Starch, $\beta$ -glucan	Cellulose
Hemicellulose	Xylose
Phenolic acid	Benzoic acid
Enzyme	Cellulase
Ash	Solslds

The feed containing the wheat bran, named *WHEATBRA*, has the composition, total mass flow rate, temperature and pressure as seen in Table 4.

Table 4. Composition, total mass flow rate, temperature, and pressure of the feed to the simplified wheat bran simulation.

Temperature	25°C
Pressure	1 bar
Total mass flow rate	100 kg/h
Mass fraction	H <sub>2</sub> O: 0.121
	Protein: 0.18
	Fat: 0.035
	Cellulose: 0.359
	Hemicellulose: 0.26
	Phenolic acid: 0.011
	Ash: 0.034

The “Methods Assistant” in Aspen Plus V11 was used for guidance in the choice of which physical property method to use for the simulation. The choice landed on the non-random two liquid model, NRTL.

### 3.1.1.1 Reactors

#### 3.1.1.1.1 Pretreatment/extraction

Saturated steam at 200°C with a mass flow rate of 50 kg/h enters the steam explosion reactor. The specifications for the steam explosion reactor can be seen in Table 5.

*Table 5. Specifications for the steam explosion block for the wheat bran process using simplified blocks.*

Aspen Plus block	RStoic <i>STEAMEXP</i>
Temperature	200 °C
Pressure	15.5 bar
Reaction and fractional conversion	Cellulose + Water → Glucose Fractional conversion of cellulose: 0.3021

After the steam explosion, the reaction mixture must be cooled, and the pressure lowered before the enzymatic hydrolysis step. The specifications for these blocks can be seen in Table 6.

*Table 6. Specifications for the cooling and valve blocks for the wheat bran process using simplified blocks.*

Aspen Plus block	Heater <i>COOLER1</i>
Temperature	50°C
Aspen Plus block	Valve <i>VALVE1</i>
Outlet pressure	1 bar

The final step in the pretreatment/extraction procedure is the enzymatic hydrolysis. To achieve the conditions as read in the literature, a stream containing water and enzyme is fed to the reactor. The specifications for the stream called *H2O+ENZY* are as follows: 50°C, 1 bar, total mass flow rate of 450.025 kg/h, mass flow of water: 450 kg/h, mass flow of enzyme: 0.025 kg/h.

In Table 7, the specifications for the enzymatic hydrolysis reactor can be seen.

*Table 7. Specifications for the enzymatic hydrolysis block for the wheat bran process using simple blocks.*

<b>Aspen Plus block</b>	<b>RStoic ENZYMHYD</b>
<b>Temperature</b>	50°C
<b>Pressure</b>	1 bar
<b>Valid phases</b>	Liquid-Only
<b>Reaction and fractional conversion</b>	Cellulose + Water → Glucose Fractional conversion of cellulose: 1

### 3.1.1.1.2 Isomerization

The isomerization reaction takes place using glucose isomerase, which is fed to the *ISOMER* reaction block with a mass flow of 2.2 g/h, a temperature of 45°C and a pressure of 1 bar. The specifications for the isomerization block are seen in Table 8.

*Table 8. Specifications for the isomerization reaction block for the simplified wheat bran process.*

<b>Aspen Plus block</b>	<b>RStoic ISOMER</b>
<b>Temperature</b>	45°C
<b>Pressure</b>	1 bar
<b>Reaction and fractional conversion</b>	Glucose → Fructose Fractional conversion of glucose: 0.42

### 3.1.1.1.3 Dehydration

The dehydration reaction is simulated to follow the method described in Sayed et al., using DMC as solvent and HCl as catalyst<sup>40</sup>. The dehydration reaction is also simulated with no reactions resulting in by-products. The DMC and HCl are fed to the reactor in separate streams, DMC at 25°C, 1 bar at a mass flow rate of 20.1 kg/h and HCl at 25°C, 1 bar and 1.65 l/h.

The specifications of the *DEHYDR* reaction block are as follows (Table 9):

Table 9. Specifications for the dehydration reaction block for the simplified wheat bran process.

Aspen Plus block	RStoic <i>DEHYDR</i>
Temperature	200°C
Pressure	15 bar
Valid phases	Vapor-liquid-liquid
Reaction and fractional conversion	Fructose → HMF + 3 Water Fractional conversion of fructose: 0.965

### 3.1.1.2 Separators

All the separations were made using the Sep block in Aspen Plus, which makes it possible to select either flow or split fractions for each component in the outlet streams to the block. The Sep block does not perform a real separation but is used as a simplified initial step. The specifications for the Sep blocks can be seen in Table 10.

Table 10. Specifications for the Sep blocks used for the wheat bran process using simplified blocks.

Block	<i>SEP-FILT</i>	<i>S-GI-H2O</i>	<i>SEP-SOL</i>	<i>SEP-HMF</i>
Function	Filter by-products from pre-treatment	Remove glucose isomerase and additional water after isomerization	Separate solvent and catalyst from reaction mixture after dehydration	Final purification of HMF
Name of specified outlet stream	<i>WB-WASTE</i>	<i>H2O+GI</i>	<i>SOL-OUT</i>	<i>HMF</i>
Specifications	Mass flow rate of water: 248 kg/h Split fraction of protein, fat, hemicellulose, phenolic acid, ash and enzyme: 1	Mass flow rate of water: 204 kg/h Split fraction of enzyme: 1	Split fraction of HCl and DMC: 1	Split fraction of HMF: 1

### 3.1.2 Simplified simulation of sugar beet pulp to HMF

The complete process flow diagram can be seen in Figure 3.

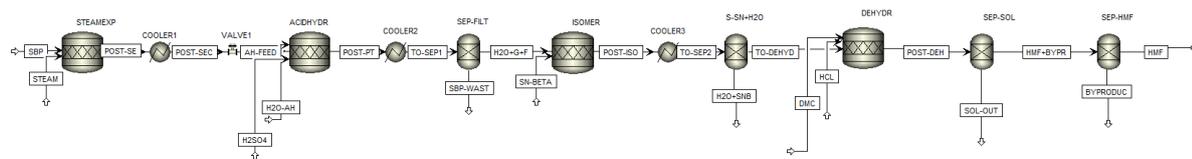


Figure 3. The complete process flow diagram for the simplified simulation of sugar beet pulp to HMF.

The simulated composition of sugar beet pulp originates from the composition in Table 2. Because of the limitations in Aspen Plus, not all components were found and had to be replaced by comparable substances. In Table 11, all the replaced components are stated. The protein is replaced by the most occurrent amino acid<sup>54</sup>.

Some of the components are collected from an in-house databank used at the Department of Chemical Engineering at Lund University, which contains biobased compounds. The compounds used from the databank are cellulase, cellulose, glucose, lignin, solsls (soluble solids) and xylan.

During the simulation, there were recurring warnings about missing property parameters for some of the different compounds. In that case, the missing values were taken from other similar compounds in the program “Database Manager – Aspen Properties V11”.

Table 11. Compounds and their replacements in the feed for the sugar beet pulp simulation using simple blocks.

Compound	Replaced with
<b>Glucan</b>	Cellulose
<b>Galactan</b>	DL-galactose
<b>Arabinan</b>	Arabinose
<b>Mannan</b>	Mannose
<b>Pectin</b>	D-galacturonic acid
<b>Protein</b>	DL-aspartic acid <sup>54</sup>
<b>Ash</b>	Solslts

The feed of sugar beet pulp is assumed to be dried, containing 90 wt% dry matter. Thus, the feed containing sugar beet pulp, named *SBP*, has the composition, total mass flow rate, temperature and pressure presented in Table 12.

The water fraction is assumed to be the fraction labelled as “Others” in Table 2, as well as the moisture content of 10 wt%.

*Table 12. Composition, total mass flow rate, temperature, and pressure of the feed to the sugar beet pulp simulation using simplified blocks.*

<b>Temperature</b>	25°C
<b>Pressure</b>	1 bar
<b>Total mass flow rate</b>	100 kg/h
<b>Mass fraction</b>	Glucan: 0.2043
	Xylan: 0.04626
	Galactan: 0.05328
	Arabinan: 0.21357
	Mannan: 0.01665
	Pectin: 0.20556
	Lignin: 0.01044
	Protein: 0.10278
	Ash: 0.02259
	H <sub>2</sub> O: 0.12457

The Methods Assistant in Aspen Plus V11 was used for guidance in the choice of which physical property method to use for the simulation. The used method in this simulation is the NRTL model.

### 3.1.2.1 Reactors

#### 3.1.2.1.1 Pretreatment/extraction

Saturated steam at 210°C with a mass flow rate of 50 kg/h enters the steam explosion reactor. The specifications for the steam explosion reactor can be seen in Table 13. As previously mentioned, the cellulose, which is the component glucan is exchanged for, is taken from an in-house databank.

Table 13. Specifications for the steam explosion block for the sugar beet pulp process using simplified blocks.

Aspen Plus block	RStoic <i>STEAMEXP</i>
Temperature	210 °C
Pressure	19.1 bar
Reaction and fractional conversion	Glucan + Water → Glucose Fractional conversion of glucan: 0.49

After the steam explosion, the reaction mixture must be cooled, and the pressure lowered before the acid hydrolysis step. The specifications for these blocks can be seen in Table 14.

Table 14. Specifications for the cooling and valve blocks in the pretreatment part of the process for the simulation with simplified blocks and sugar beet pulp as the raw material.

Aspen Plus block	Heater <i>COOLER1</i>
Temperature	50°C
Aspen Plus block	Valve <i>VALVE1</i>
Outlet pressure	1 bar

The final step in the pretreatment is the acid hydrolysis. To achieve the conditions as read in the literature, two separate streams containing water and H<sub>2</sub>SO<sub>4</sub> respectively are fed to the reactor. The specifications for the stream called *H2O-AH* are as follows: 25°C, 1 bar, total volume flow rate of 1.45 m<sup>3</sup>/h, mass fraction of water = 1. The specifications for the stream called *H2SO4* are as follows: 25°C, 1 bar, total volume flow rate of 8 l/h, mass fraction of H<sub>2</sub>SO<sub>4</sub> = 1. In Table 15, the specifications for the enzymatic hydrolysis reactor can be seen. It is assumed that both glucose and fructose is produced by acid hydrolysis in the simplified process.

Table 15. Specifications for the acid hydrolysis block for the sugar beet pulp process using simplified blocks.

Aspen Plus block	RStoic <i>ACIDHYDR</i>
Temperature	121°C
Pressure	3 bar
Reaction and fractional conversion	2 Glucan + 2 Water → Glucose + Fructose Fractional conversion of glucan: 1

### 3.1.2.1.2 Isomerization

After the acid hydrolysis, the reaction mixture is cooled in a heater block called *COOLER2* to 50°C.

The isomerization reaction takes place using Sn- $\beta$ , which is fed to the *ISOMER* reaction block with a mole flow of 1.88 mol/h, a temperature of 25°C and a pressure of 2 bar. The specifications for the isomerization block are seen in Table 16.

Table 16. Specifications for the isomerization reaction block for the sugar beet pulp process using simple blocks.

Aspen Plus block	RStoic <i>ISOMER</i>
Temperature	110°C
Pressure	2 bar
Reaction and fractional conversion	Glucose → Fructose Fractional conversion of glucose: 0.31 Glucose → Mannose Fractional conversion of glucose: 0.09

Then, the reaction mixture was cooled again to 50°C in a heater block called *COOLER3*.

### 3.1.2.1.3 Dehydration

The dehydration reaction is simulated to follow the method described in Sayed et al., using DMC as solvent and HCl as catalyst<sup>40</sup>. The dehydration reaction is also simulated with no reactions resulting in by-products. The DMC and HCl are fed to the reactor in separate streams, DMC at 25°C, 1 bar at a mass flow rate of 5.02 kg/h and HCl at 25°C, 1 bar and 0.59 l/h.

The specifications of the *DEHYDR* reaction block are as follows (Table 17):

Table 17. Specifications for the dehydration reaction block for the sugar beet pulp process using simple blocks.

Aspen Plus block	RStoic <i>DEHYDR</i>
Temperature	200°C
Pressure	15 bar
Valid phases	Vapor-liquid-liquid
Reaction and fractional conversion	Fructose → HMF + 3 Water Fractional conversion of fructose: 0.965

### 3.1.2.2 Separators

All the separations were made using the Sep block in Aspen Plus, which makes it possible to select either flow or split fractions for each component in the outlet streams to the block. The Sep block does not perform a real separation but is used as a simplified initial step. The specifications for the Sep blocks can be seen in Table 18.

Table 18. Specifications for the Sep blocks used for the sugar beet pulp process using simple blocks.

Block	<i>SEP-FILT</i>	<i>S-SN+H2O</i>	<i>SEP-SOL</i>	<i>SEP-HMF</i>
Function	Filter away by-products from pretreatment	Remove Sn- $\beta$ and additional water after isomerization	Separate solvent and catalyst from reaction mixture after dehydration	Final purification of HMF
Name of specified outlet stream	<i>SBP-WAST</i>	<i>H2O+SNB</i>	<i>SOL-OUT</i>	<i>BYPRODUC</i>
Specifications	Mass flow rate of water: 1355 kg/h Split fraction of xylan, galactan, arabinan, mannan, pectin, lignin, protein, ash and H <sub>2</sub> SO <sub>4</sub> : 1	Mass flow rate of water: 132.4 kg/h Split fraction of Sn- $\beta$ : 1	Split fraction of HCl and DMC: 1	Split fraction of water, glucose, fructose, and mannose: 1

## 3.2 Process simulation using advanced blocks

To achieve a more complete and realistic simulation with more resemblance to the literature and reality, a process simulation with advanced blocks was made. The method used is the “Onion model”, meaning that the process design starts with the reactors, then the separation and recycle system, then the heat exchanger system, etc<sup>55</sup>. The physical property method used for the simulation is NRTL.

### 3.2.1 Reactors

For the advanced blocks simulation, all the reactors used are “RStoic” blocks. No reaction kinetics were used in the simulation. An effort was made to simulate all combinations of reactors on the three different converting steps of the block flow diagram. Therefore, the pretreatment step consists of steam explosion and acid hydrolysis or enzymatic hydrolysis, the isomerization step consists of chemical catalytic isomerization or enzymatic isomerization and the dehydration step consists of biphasic dehydration or one of two types of dehydration using heterogenic catalysts. The simulation resulted in a total of 12 different outflow streams each for the two raw materials, wheat bran and sugar beet pulp, respectively. The composition of the outflow streams and their HMF content can be used to evaluate which processes to work further on and add separation units, heat exchangers etc. Not all the 12 processes could be used for further process simulations because of time constraints.

The purpose of the advanced blocks reactor simulation is to evaluate how the reactors and combination of reactors perform without relying on the separation system. Between each converting step in the flowsheet, a new stream was added with the same composition as the outflow from the step before, but without the components that are to be removed by separation in coming steps of the process design.

The only times where separation units were used when performing the advanced blocks reactor simulation is when specific concentrations of components were needed to resemble those in the literature. Likewise, heat exchangers were only used to cool down streams to normal conditions, to be able to know the volumetric flows of streams and thus be able to calculate specific volumetric concentrations like the ones used in the literature. All calculations made to perform the reactor simulation using advanced blocks can be seen in Appendix C and Appendix D.

The simulation is more complete than the simple blocks simulation in the sense that reactions forming by-products have also been included in the steps where such formation is applicable.

To get an idea of the layout of the reactor simulation, the complete flowsheet for the advanced blocks reactor simulation is presented in Figure 4. More detailed pictures of the sections are shown in other parts of the report.

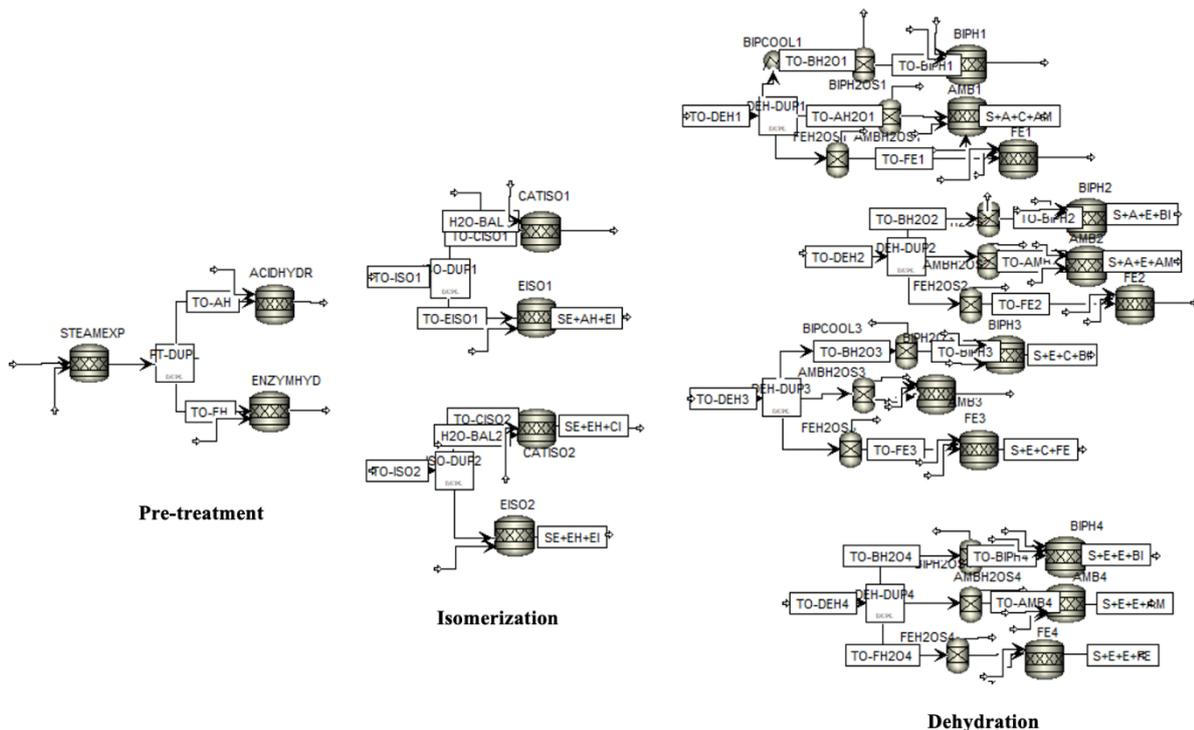


Figure 4. Complete view of the advanced blocks simulation of the reactors. Two separate simulations with the same layout were made for wheat bran and sugar beet pulp, respectively.

### 3.2.1.1 Reactor simulation using wheat bran

The simulated composition of wheat bran proceeds from the composition stated in Table 1, with some modifications. Because of limitations in Aspen Plus, not all the components were found and had to be replaced with comparable substances. In Table 19, all the replaced components are stated. The fat and protein fractions are replaced by the most occurrent fatty acid and amino acid respectively<sup>52, 53</sup>. The feed containing the wheat bran, named *WHEATBRA*, has the composition, total mass flow rate, temperature and pressure as seen in Table 19.

Some of the components are collected from an in-house databank used at the Department of Chemical Engineering at Lund University, which contains biobased compounds. The compounds used from the databank are cellulase, cellulose, glucose, solunkn (unknown soluble solids) and xylose.

During the simulation, there were recurring warnings about missing property parameters for some of the different compounds. In that case, the missing values were taken from other similar compounds in the program “Database Manager – Aspen Properties V11”.

Table 19. Left: Compounds and their replacements in the feed for the wheat bran simulation using advanced blocks. Right: Composition, total mass flow rate, temperature, and pressure of the feed to the wheat bran simulation using advanced blocks.

<b>Compound</b>	<b>Replaced with</b>	<b>Temperature</b>	25°C
<b>Protein</b>	DL-glutamic acid <sup>52</sup>	<b>Pressure</b>	1 bar
<b>Fat</b>	Linoleic acid <sup>53</sup>	<b>Total mass flow rate</b>	1000 kg/h
<b>Starch</b>	Glucose	<b>Mass fraction</b>	H <sub>2</sub> O: 0.121
<b>Arabinoxylan</b>	Xylose		Protein: 0.158
<b>β-glucan</b>	Glucose		Fat: 0.037
<b>Phenolic acid</b>	Ferulic acid <sup>56</sup>		Starch: 0.249
<b>Ash</b>	Solunkn		Cellulose: 0.11
<b>Enzyme</b>	Cellulase		Arabinoxylan: 0.231
<b>Heterogenic catalyst</b>	Cellulase (type set as solid)		β-glucan: 0.025
			Phenolic acid: 0.011
			Ash: 0.058

### 3.2.1.1.1 Pretreatment/extraction in the wheat bran simulation

The pretreatment section of the flowsheet can be seen in Figure 5.

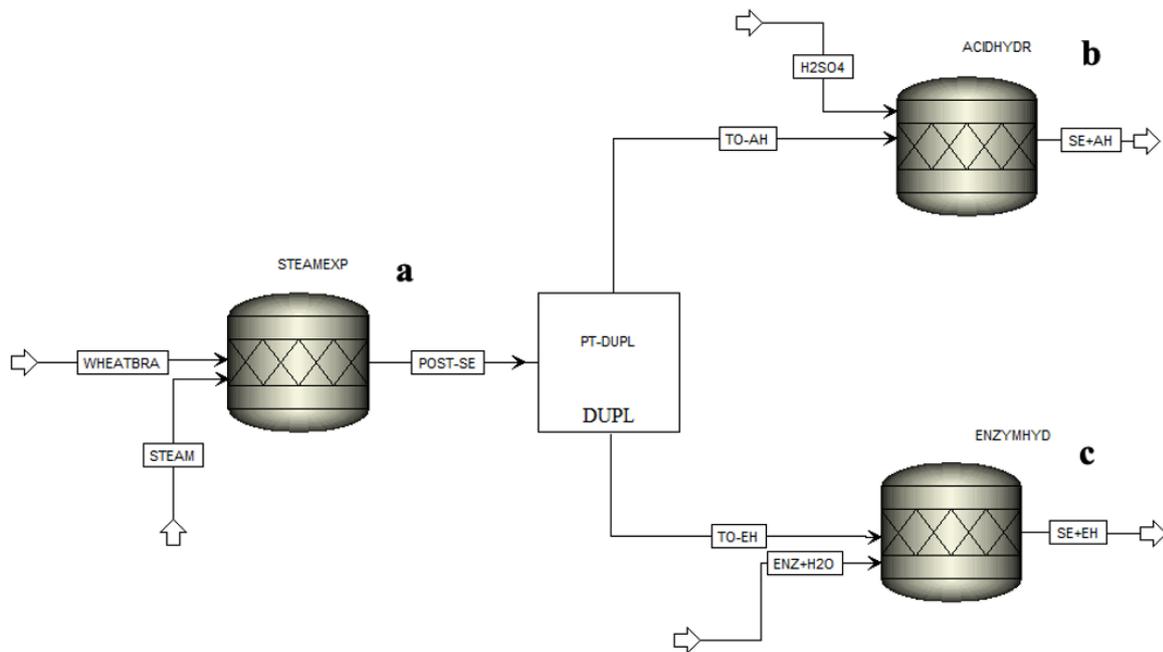


Figure 5. The pretreatment section of the flowsheet for the wheat bran reactor simulation using advanced blocks. a) Steam explosion; b) Acid hydrolysis; c) Enzymatic hydrolysis.

The wheat bran is fed to the pretreatment section of the flowsheet, which consists of steam explosion and either acid hydrolysis or enzymatic hydrolysis. The specifications of the streams entering these three reactors can be seen in Table 20, while the specifications for the reactors can be seen in Table 21. The mass flow rate of steam was obtained by a design specification stating that the temperature in the outflow of the reactor should be 200°C by varying the mass flow of steam entering the steam explosion step. The resulting mass flow rate was the one used throughout the rest of the simulations.

Table 20. Specifications of streams entering blocks in the pretreatment section of the flowsheet for the reactor simulation of wheat bran process using advanced blocks.

<b>Name of stream</b>	<b><i>STEAM</i></b>	<b><i>H2SO4</i></b>	<b><i>ENZ+H2O</i></b>
<b>To block</b>	<i>STEAMEXP</i>	<i>ACIDHYDR</i>	<i>ENZYMHYD</i>
<b>Temperature</b>	200°C	25°C	25°C
<b>Pressure</b>		1 bar	1 bar
<b>Vapor fraction</b>	1		
<b>Total flow</b>	285 kg/h	51.4 kg/h	4715.178 kg/h
<b>Composition</b>	Mass fraction	Mass fraction	Mass flow
	Water: 1	Water: 0.5	Water: 4715 kg/h
		H <sub>2</sub> SO <sub>4</sub> : 0.5	Enzyme: 0.178 kg/h

Table 21. Specifications for the pretreatment reactor blocks for the wheat bran process using advanced blocks.

Name of block	<i>STEAMEXP</i>	<i>ACIDHYDR</i>	<i>ENZYMHYD</i>
Temperature	200°C	170°C	50°C
Pressure		8 bar	1 bar
Duty	0 kW		
Valid phases	Vapor-Liquid	Vapor-Liquid	Liquid-Only
Reactions	Starch + Water → 1.1 Glucose	Cellulose + Water → Glucose	Starch + Water → 1.1 Glucose
	Cellulose + Water → Glucose	$\beta$ -glucan + Water → 1.1 Glucose	
	$\beta$ -glucan + Water → 1.1 Glucose	Arabinoxylan + Wa- ter → 1.12 Xylose	
	Arabinoxylan + Wa- ter → 1.12 Xylose	Arabinoxylan + Wa- ter → 1.12 Arabinose	
	Arabinoxylan + Wa- ter → 1.12 Arabinose		
Fractional conver- sion	Starch: 0.285  Cellulose: 0.2825  $\beta$ -glucan: 0.285 Arabinoxylan (xy- lose): 0.000536 Arabinoxylan (arabi- nose): 0.000182	Cellulose: 0.49  $\beta$ -glucan: 0.4944  Arabinoxylan (xy- lose): 0.2715 Arabinoxylan (arabi- nose): 0.22	Starch: 1

### 3.2.1.1.2 Isomerization in the wheat bran simulation

The isomerization part of the flowsheet can be seen in Figure 6.

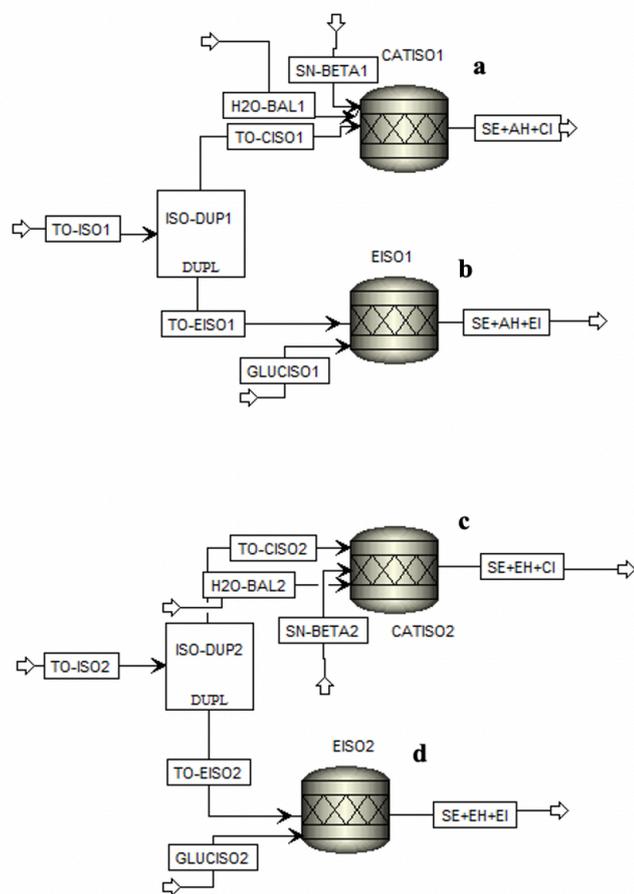


Figure 6. The isomerization section of the flowsheet for the wheat bran reactor simulation using advanced blocks. a) and c) Catalytic isomerization using Sn- $\beta$ ; b) and d) Enzymatic isomerization.

After the pretreatment, the outflows are taken to either chemical catalytic isomerization using Sn- $\beta$  or enzymatic isomerization using glucose isomerase. Specifications for the streams entering this part of the flowsheet can be seen in Table 22, and specifications for the isomerization reactors can be seen in Table 23.

Table 22. Specifications of streams entering blocks in the isomerization section of the flow-sheet for the reactor simulation of wheat bran process using advanced blocks.

Name of stream	<i>H2O-BAL1</i>	<i>SN-BETA1</i>	<i>H2O-BAL2</i>	<i>SN-BETA2</i>	<i>GLU-CIS01</i>	<i>GLU-CIS02</i>
To block	<i>CATISO1</i>		<i>CATISO2</i>		<i>EISO1</i>	<i>EISO2</i>
Temperature	25°C	25°C	25°C	25°C	25°C	25°C
Pressure	1 bar	1 bar	1 bar	1 bar	1 bar	1 bar
Total flow	1156.44 kg/h	19.2185 mol/h	2108.44 kg/h	35.1098 mol/h	9.62 g/h	17.6 g/h
Fraction	Mass	Mole	Mass	Mole	Mass	Mass
	Water: 1	Hetero- genic cata- lyst: 1	Water: 1	Hetero- genic cata- lyst: 1	Enzyme: 1	Enzyme: 1

Table 23. Specifications for the isomerization reactor blocks for the wheat bran process using advanced blocks.

Name of block	<i>CATISO1, CATISO2</i>	<i>EISO1, EISO2</i>
Temperature	110°C	45°C
Pressure	1.4 bar	1 bar
Valid phases	Vapor-Liquid	Liquid-Only
Reactions	Glucose → Fructose Glucose → Mannose	Glucose → Fructose
Fractional conversion	Glucose (fructose): 0.31 Glucose (mannose): 0.09	Glucose: 0.42

### 3.2.1.1.3 Dehydration in the wheat bran simulation

One part of the dehydration section of the flowsheet can be seen in Figure 7.

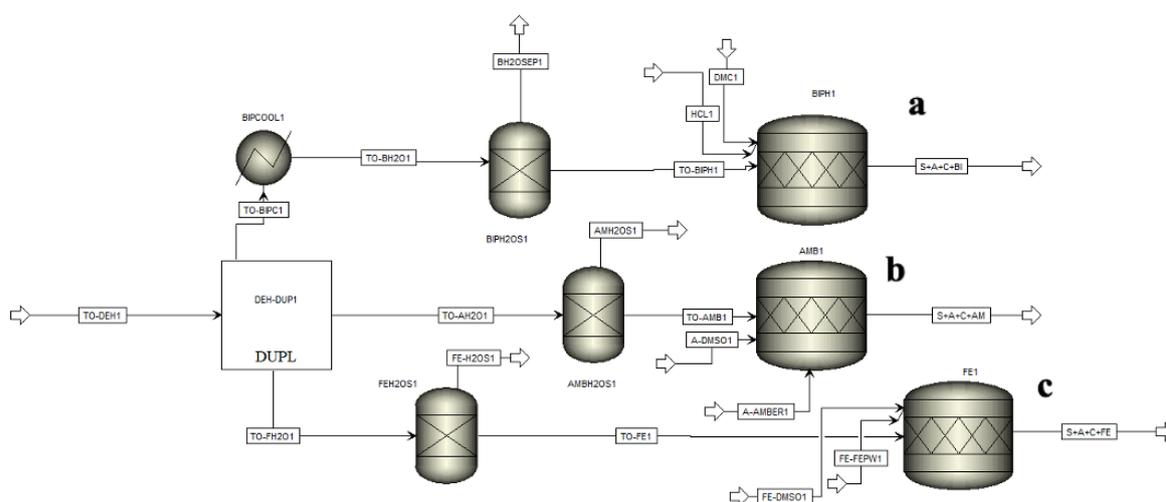


Figure 7. One part of the dehydration section of the flowsheet for the wheat bran reactor simulation using advanced blocks. a) Biphasic dehydration; b) Dehydration using Amberlyst 15 powder; c) Dehydration using  $\text{FePW}_{12}\text{O}_{40}$ .

After isomerization of glucose to fructose, the outflowing streams are taken to one of three dehydration reactors. Specifications of the streams containing solvent and catalyst entering the reactors can be seen in Table 24, Table 25 and Table 26.

Table 24. Specifications of the streams entering the biphasic dehydration reaction blocks for the reactor simulation of the wheat bran process using advanced blocks.

Name of stream	DMC1	HCL1	DMC2	HCL2	DMC3	HCL3	DMC4	HCL4
To block	BIPH1		BIPH2		BIPH3		BIPH4	
Temperature	25°C	25°C	25°C	25°C	25°C	25°C	25°C	25°C
Pressure	1 bar	1 bar						
Total flow rate	18.2 kg/h	6.86 l/h	39.4 kg/h	9.28 l/h	16.8 kg/h	12.5 l/h	78.3 kg/h	17 l/h
Composition	Mass fraction	Mole conc.						
	DMC: 1	HCl: 6 mol/l						

Table 25. Specifications of the DMSO-streams entering the heterogeneous catalyst dehydration reaction blocks for the reactor simulation of the wheat bran process using advanced blocks.

<b>Name of stream</b>	<b><i>A-DMSO1, FE-DMSO1</i></b>	<b><i>A-DMSO2, FE-DMSO2</i></b>	<b><i>A-DMSO3, FE-DMSO3</i></b>	<b><i>A-DMSO4, FE-DMSO4</i></b>
<b>To block</b>	<i>AMB1, FE1</i>	<i>AMB2, FE2</i>	<i>AMB3, FE3</i>	<i>AMB4, FE4</i>
<b>Temperature</b>	25°C	25°C	25°C	25°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	1616 kg/h	2250.5 kg/h	2952 kg/h	4111.4 kg/h
<b>Mass fraction</b>	DMSO: 1	DMSO: 1	DMSO: 1	DMSO: 1

Table 26. Specifications of the catalyst streams entering the heterogeneous catalyst dehydration reaction blocks for the reactor simulation of the wheat bran process using advanced blocks.

<b>Name of stream</b>	<b><i>A-AMBER1, FE-FEPW1</i></b>	<b><i>A-AMBER2, FE-FEPW2</i></b>	<b><i>A-AMBER3, FE-FEPW3</i></b>	<b><i>A-AMBER4, FE-FEPW4</i></b>
<b>To block</b>	<i>AMB1, FE1</i>	<i>AMB2, FE2</i>	<i>AMB3, FE3</i>	<i>AMB4, FE4</i>
<b>Temperature</b>	25°C	25°C	25°C	25°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	3.22 kg/h	4.36 kg/h	5.88 kg/h	7.97 kg/h
<b>Mass fraction</b>	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1

Additional information about heater blocks etc. present in this step can be seen in Appendix B.1.1.

The specifications of the dehydration reactors can be seen in Table 27.

Table 27. Specifications for the dehydration reactor blocks for the wheat bran process using advanced blocks.

Name of block	<i>BIPH1-4</i>	<i>AMB1-4</i>	<i>FE1-4</i>
Temperature	200°C	120°C	120°C
Pressure	15 bar	2 bar	2 bar
Valid phases	Vapor-Liquid-Liquid	Vapor-Liquid	Vapor-Liquid
Reactions	Fructose → HMF + 3 Water  HMF + 2 Water → Formic acid + Levulinic acid	Fructose → HMF + 3 Water	Fructose → HMF + 3 Water  HMF + 2 Water → Formic acid + Levulinic acid
Fractional conversion	Fructose: 0.965  HMF: 0.09	Fructose: 1	Fructose: 1  HMF: 0.03

#### 3.2.1.1.4 Assumptions for the wheat bran reactor simulation

To get the reactor simulation working properly, the following assumptions were made. It is assumed that NRTL can be used as the physical property method even though the pressure in the steam explosion reactor is above 10 bar. Sn-β, Amberlyst 15 powder, FePW<sub>12</sub>O<sub>40</sub> and the enzymes were modelled as cellulase taken from the database containing biobased compounds. When the catalysts Sn-β, Amberlyst 15 powder or FePW<sub>12</sub>O<sub>40</sub> were used, the type was changed from conventional to solid. It is assumed that both xylose and arabinose is formed from arabinoxylan. No by-products are assumed to be formed during the enzymatic hydrolysis step because of the specificity of the enzyme<sup>14</sup>. In the enzymatic hydrolysis, there was not enough starch left to be able to form all the glucose that was formed in the literature. Therefore, the fractional conversion of starch was set to 1.<sup>14</sup> In the two reactors where DMSO is used as solvent, the source states that water is removed continuously<sup>3</sup>, however, this is not simulated. It is assumed that the entire stream entering the biphasic reactor is water, to be able to calculate the flows of DMSO and HCl.

### 3.2.1.2 Reactor simulation using sugar beet pulp

The simulated composition of sugar beet pulp originates from the composition in Table 2. Because of limitations in Aspen Plus, not all components were found and had to be replaced by comparable substances. In Table 28, all the replaced components are stated. The protein is replaced by the most occurrent amino acid<sup>54</sup>.

Some of the components are collected from an in-house databank used at the Department of Chemical Engineering at Lund University, which contains biobased compounds. The compounds used from the databank are cellulase, cellulose, glucose, lignin, solunkn (unknown soluble solids), xylan and xylose.

During the simulation, there were recurring warnings about missing property parameters for some of the different compounds. In that case, the missing values were taken from other similar compounds in the program “Database Manager – Aspen Properties V11”.

The feed of sugar beet pulp is assumed to be dried, containing 90 wt% dry matter. Thus, the feed containing sugar beet pulp, named *SUGARBEP*, has the composition, total mass flow rate, temperature and pressure as seen in Table 29. The water fraction is assumed to be the 10 wt% moisture content. Because fructose is formed during the acid hydrolysis, the fraction labelled as “Others” in Table 2 is set as sucrose in the advanced blocks simulation.

Table 28. Compounds and their replacements in the feed for the sugar beet pulp simulation using advanced blocks.

Compound	Replaced with
Glucan	Cellulose
Galactan	DL-galactose
Arabinan	Arabinose
Mannan	Mannose
Pectin	D-galacturonic acid
Protein	DL-aspartic acid <sup>54</sup>
Ash	Solunkn
Enzyme	Cellulase
Heterogenic catalyst	Cellulase (type set as solid)

*Table 29. Composition, total mass flow rate, temperature, and pressure of the feed to the sugar beet pulp simulation using more advanced blocks.*

<b>Temperature</b>	25°C
<b>Pressure</b>	1 bar
<b>Total mass flow rate</b>	1000 kg/h
<b>Mass fraction</b>	Glucan: 0.2043
	Xylan: 0.04626
	Galactan: 0.05328
	Arabinan: 0.21357
	Mannan: 0.01665
	Pectin: 0.20556
	Lignin: 0.01044
	Protein: 0.10278
	Ash: 0.02259
	Sucrose: 0.02457
	Water: 0.1

### 3.2.1.2.1 Pretreatment/extraction in the sugar beet pulp simulation

The pretreatment section of the flowsheet can be seen in Figure 8.

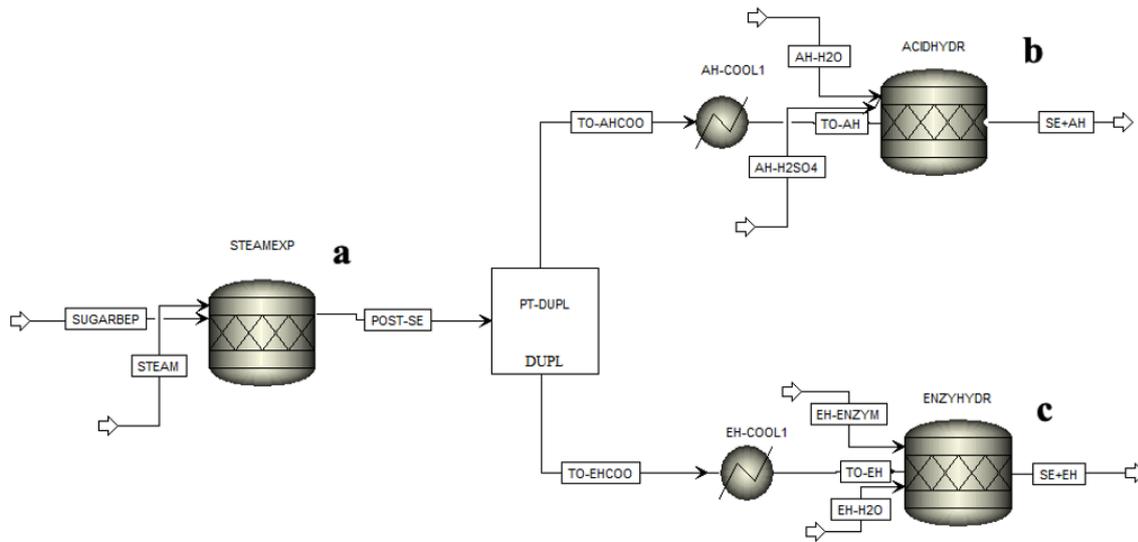


Figure 8. The pretreatment section of the flowsheet for the sugar beet pulp reactor simulation using advanced blocks. a) Steam explosion; b) Acid hydrolysis; c) Enzymatic hydrolysis.

The sugar beet pulp is fed to the pretreatment section of the flowsheet, which consists of steam explosion and either acid hydrolysis or enzymatic hydrolysis. The specifications of the streams entering these three reactors can be seen in Table 30. The specifications for the reactors can be seen in Table 31. The mass flow rate of the *STEAM* stream was obtained by a design specification stating that the temperature in the outflow of the reactor should be 210°C by varying the mass flow of steam entering the steam explosion step. The resulting mass flow rate was the one used throughout the rest of the simulations.

Table 30. Specifications of the streams entering blocks in the pretreatment section of the flowsheet for the reactor simulation of sugar beet pulp process using advanced blocks.

Name of stream	<i>STEAM</i>	<i>AH-H2O</i>	<i>AH-H2SO4</i>	<i>EH-ENZYM</i>	<i>EH-H2O</i>
To block	<i>STEAMEXP</i>	<i>ACIDHYDR</i>	<i>ACIDHYDR</i>	<i>ENZYHYDR</i>	<i>ENZYHYDR</i>
Temperature	210°C	25°C	25°C	25°C	25°C
Pressure		1 bar	1 bar	1 bar	1 bar
Vapor fraction	1				
Total flow rate	285 kg/h	5.44 m <sup>3</sup> /h	33.4 l/h	18.4 l/h	8.77 m <sup>3</sup> /h
Mass fraction	Water: 1	Water: 1	H <sub>2</sub> SO <sub>4</sub> : 1	Enzyme: 1	Water: 1

Additional information about heater blocks present in this step can be seen in Appendix B.2.1.

Table 31. Specifications for the pretreatment reactor blocks for the sugar beet pulp process using advanced blocks.

Name of block	<i>STEAMEXP</i>	<i>ACIDHYDR</i>	<i>ENZYHYDR</i>
<b>Temperature</b>	210°C	121°C	50°C
<b>Pressure</b>		2 bar	1 bar
<b>Duty</b>	0 kW		
<b>Valid phases</b>	Vapor-Liquid	Vapor-Liquid	Liquid-Only
<b>Reactions</b>	Glucan + Water → 1.1 Glucose  Pectin + Water → 1.4133 Arabinose	Sucrose + Water → Glucose + Fructose  Glucan + Water → Glucose  Glucan + Water → Fructose  Xylan + Water → Xylose  Galactan + Water → 1.1 Galactose	Glucan + Water → Glucose
<b>Fractional conversion</b>	Glucan: 0.1  Pectin: 0.97	Sucrose: 1  Glucan (glucose): 0.1784  Glucan (fructose): 0.1916  Xylan: 0.0997  Galactan: 0.2534	Glucan: 0.47

### 3.2.1.2.2 Isomerization in the sugar beet pulp simulation

The isomerization section of the flowsheet can be seen in Figure 9.

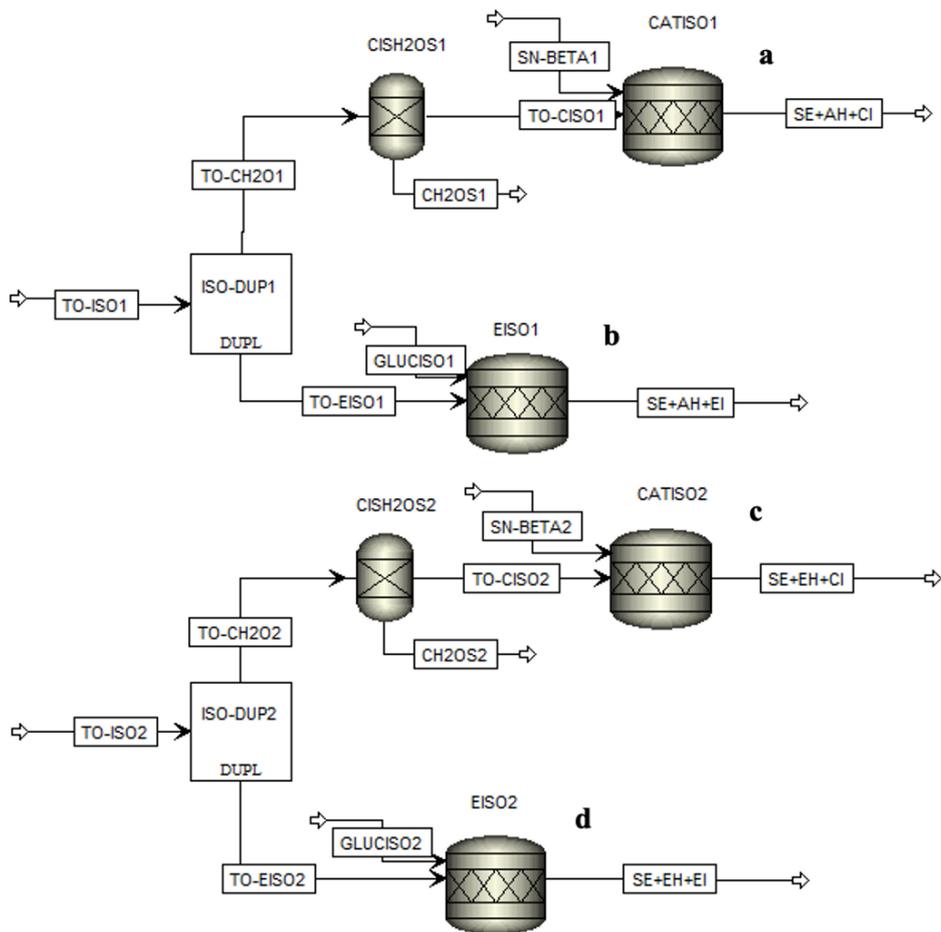


Figure 9. The isomerization section of the flowsheet for the sugar beet pulp reactor simulation using advanced blocks. a) and c) Catalytic isomerization; b) and d) Enzymatic isomerization.

After the pretreatment, the outflows are taken to either chemical catalytic isomerization using Sn- $\beta$  or enzymatic isomerization using glucose isomerase. Specifications for the streams entering this part of the flowsheet can be seen in Table 32, while specifications for the isomerization reactors can be seen in Table 33.

Table 32. Specifications of the streams entering blocks in the isomerization section of the flowsheet for the reactor simulation of the sugar beet pulp process using advanced blocks.

<b>Name of stream</b>	<b><i>SN-BETA1</i></b>	<b><i>SN-BETA2</i></b>	<b><i>GLUCISO1</i></b>	<b><i>GLUCISO2</i></b>
<b>To block</b>	<i>CATISO1</i>	<i>CATISO2</i>	<i>EISO1</i>	<i>EISO2</i>
<b>Temperature</b>	25°C	25°C	25°C	25°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	8 mol/h	13.18 mol/h	4 g/h	6.6 g/h
<b>Fraction</b>	Mole	Mole	Mass	Mass
	Heterogenic catalyst: 1	Heterogenic catalyst: 1	Enzyme: 1	Enzyme: 1

Additional information about Sep blocks present in this step can be seen in Appendix B.2.1.

Table 33. Specifications for the isomerization reactor blocks for the sugar beet pulp process using advanced blocks.

<b>Name of block</b>	<b><i>CATISO1, CATISO2</i></b>	<b><i>EISO1, EISO2</i></b>
<b>Temperature</b>	110°C	45°C
<b>Pressure</b>	1.4 bar	1 bar
<b>Valid phases</b>	Vapor-Liquid	Liquid-Only
<b>Reactions</b>	Glucose $\rightarrow$ Fructose Glucose $\rightarrow$ Mannose	Glucose $\rightarrow$ Fructose
<b>Fractional conversion</b>	Glucose (fructose): 0.31 Glucose (mannose): 0.09	Glucose: 0.42

### 3.2.1.2.3 Dehydration in the sugar beet pulp simulation

One part of the dehydration section of the flowsheet can be seen in Figure 10.

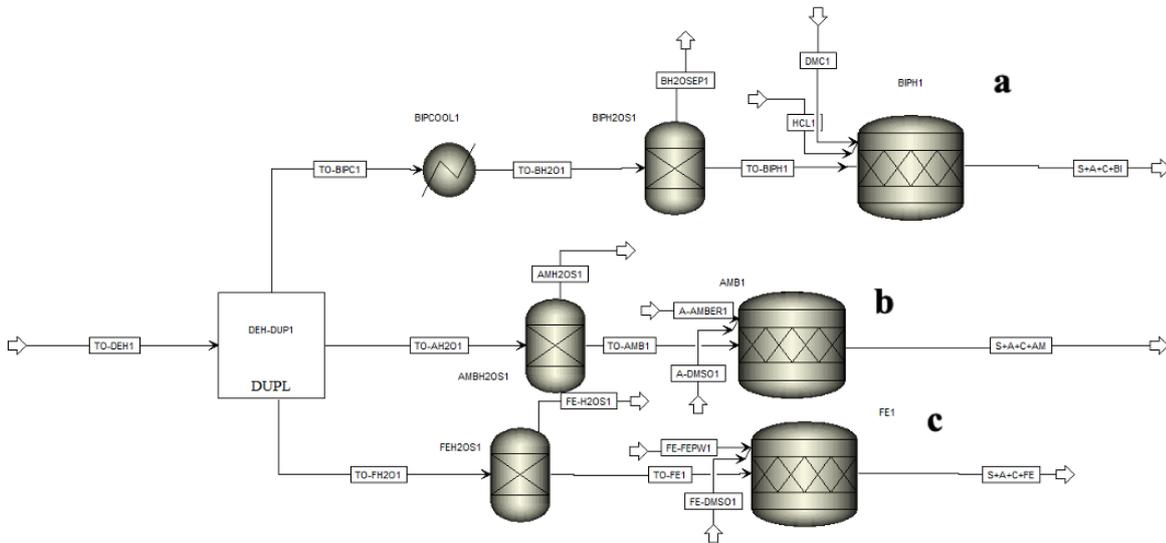


Figure 10. One part of the dehydration section of the flowsheet for the sugar beet pulp reactor simulation using advanced blocks. a) Biphasic dehydration; b) Dehydration using Amberlyst 15 powder; c) Dehydration using  $FePW_{12}O_{40}$ .

After isomerization of glucose to fructose, the outflowing streams are taken to one of three dehydration reactors. Specifications of the streams containing solvent and catalyst entering the reactors can be seen in Table 34, Table 35 and Table 36.

Table 34. Specifications of the streams entering the biphasic dehydration reaction blocks for the reactor simulation of the sugar beet pulp process using advanced blocks.

Name of stream	DMC1	HCL1	DMC2	HCL2	DMC3	HCL3	DMC4	HCL4
To block	BIPH1		BIPH2		BIPH3		BIPH4	
Temperature	25°C	25°C	25°C	25°C	25°C	25°C	25°C	25°C
Pressure	1 bar	1 bar						
Total flow rate	53.4 kg/h	9.5 l/h	63.4 kg/h	10.5 l/h	14.5 kg/h	4.7 l/h	29.1 kg/h	6.3 l/h
Composition	Mass fraction	Mole conc. HCl: 6 mol/l	Mass fraction	Mole conc. HCl: 6 mol/l	Mass fraction	Mole conc. HCl: 6 mol/l	Mass fraction	Mole conc. HCl: 6 mol/l
	DMC: 1		DMC: 1		DMC: 1		DMC: 1	

Table 35. Specifications of the DMSO-streams entering the heterogeneous catalyst dehydration reaction blocks for the reactor simulation of the sugar beet pulp process using advanced blocks.

<b>Name of stream</b>	<i>A-DMSO1, FE-DMSO1</i>	<i>A-DMSO2, FE-DMSO2</i>	<i>A-DMSO3, FE-DMSO3</i>	<i>A-DMSO4, FE-DMSO4</i>
<b>To block</b>	<i>AMB1, FE1</i>	<i>AMB2, FE2</i>	<i>AMB3, FE3</i>	<i>AMB4, FE4</i>
<b>Temperature</b>	25°C	25°C	25°C	25°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	2356 kg/h	2621 kg/h	1108 kg/h	1534 kg/h
<b>Mass fraction</b>	DMSO: 1	DMSO: 1	DMSO: 1	DMSO: 1

Table 36. Specifications of the catalyst streams entering the heterogeneous catalyst dehydration reaction blocks for the reactor simulation of the sugar beet pulp process using advanced blocks.

<b>Name of stream</b>	<i>A-AMBER1, FE-FEPW1</i>	<i>A-AMBER2, FE-FEPW2</i>	<i>A-AMBER3, FE-FEPW3</i>	<i>A-AMBER4, FE-FEPW4</i>
<b>To block</b>	<i>AMB1, FE1</i>	<i>AMB2, FE2</i>	<i>AMB3, FE3</i>	<i>AMB4, FE4</i>
<b>Temperature</b>	25°C	25°C	25°C	25°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	4.47 kg/h	4.94 kg/h	2.21 kg/h	2.97 kg/h
<b>Mass fraction</b>	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1	Heterogeneous catalyst: 1

Additional information about heater blocks etc. present in this step can be seen in Appendix B.2.1.

The specifications of the dehydration reactors can be seen in Table 37.

Table 37. Specifications for the dehydration reactor blocks for the sugar beet pulp process using more advanced blocks.

Name of block	<i>BIPH1-4</i>	<i>AMB1-4</i>	<i>FE1-4</i>
Temperature	200°C	120°C	120°C
Pressure	15 bar	2 bar	2 bar
Valid phases	Vapor-Liquid-Liquid	Vapor-Liquid	Vapor-Liquid
Reactions	Fructose → HMF + 3 Water  HMF + 2 Water → Formic acid + Levulinic acid	Fructose → HMF + 3 Water	Fructose → HMF + 3 Water  HMF + 2 Water → Formic acid + Levulinic acid
Fractional conversion	Fructose: 0.965  HMF: 0.09	Fructose: 1	Fructose: 1  HMF: 0.03

#### 3.2.1.2.4 Assumptions for the sugar beet pulp reactor simulation

To get the reactor simulation working properly, the following assumptions were made. It is assumed that NRTL can be used as the physical property method even though the pressure in the steam explosion reactor is above 10 bar. Sn- $\beta$ , Amberlyst 15 powder, FePW<sub>12</sub>O<sub>40</sub> and the enzymes were modelled as cellulase taken from the database containing biobased compounds. When the catalysts Sn- $\beta$ , Amberlyst 15 powder or FePW<sub>12</sub>O<sub>40</sub> were used, the type was changed from conventional to solid. The dry matter content in the raw material feed stream is assumed to be 90 wt.%, and the fraction labelled “Others” in Table 2 is assumed to be sucrose. In the steam explosion step, only glucan and pectin are assumed to react to glucose and arabinose respectively. In the acid hydrolysis reactor, fructose is formed to the same extent to that found in the literature. Because of the sucrose in the raw material not being present in large enough amounts to form the entirety of the fructose, the fructose is also assumed to be formed from glucan. It is assumed that no formation of by-products is present in the enzymatic hydrolysis<sup>17</sup>. The feed of fructose to the isomerization reactors is assumed to not affect the conversion of glucose to fructose and mannose or glucose to fructose. In the two reactors where DMSO is used as solvent, the source states that water is removed continuously<sup>3</sup>, however, this is not simulated. It is assumed that the entire stream entering the biphasic reactor is water, to be able to calculate the flows of DMSO and HCl.

### 3.2.1.3 *Processes which will be used in further simulations*

#### 3.2.1.3.1 Wheat bran

For wheat bran, the highest yields of HMF and fructose were obtained by the process with steam explosion, enzymatic hydrolysis, enzymatic isomerization, and a dehydration reactor. The dehydration reactor that exhibited the highest yield was the one that used Amberlyst 15-powder as heterogeneous catalyst, because of its 100% conversion, yield and selectivity, which means that no by-products are formed, and all fructose is converted to HMF. However, this reactor uses DMSO as solvent, which is hard to separate from the rest of the reaction mixture. Because of this, the process that will be used in the further simulations is the combination of steam explosion, enzymatic hydrolysis, enzymatic isomerization, and biphasic dehydration using DMC and HCl. The enzymatic conversion steps also have the added benefit of fewer by-products and lower temperatures, which can affect the energy used for heating the system.

#### 3.2.1.3.2 Sugar beet pulp

For sugar beet pulp, the highest yields of HMF and fructose were obtained by the process with steam explosion, acid hydrolysis, enzymatic isomerization, and a dehydration reactor. The most efficient dehydration reactor was the one that used Amberlyst 15-powder as heterogeneous catalyst because of the same reasons mentioned for the wheat bran process. Because of DMSO being used as a solvent in the Amberlyst 15-powder reactor, it will not be used in further simulations. Instead, the process that will be used in further simulations is the combination of steam explosion, acid hydrolysis, enzymatic isomerization, and biphasic dehydration using DMC and HCl. The acid hydrolysis has an advantage of fructose formation for the sugar beet pulp simulation, which adds significantly to the amount of formed fructose in the process.

### 3.2.2 Separation and recirculation

As previously stated, the reactor simulation did not include any separation steps other than Sep-blocks to achieve the same conditions as those described in the literature which is the foundation of this thesis. The reactor simulation was not a complete flow system in the sense that the blocks in the different sections were not connected to each other, as the separation also was performed by simply copying the conditions of the streams and leaving out unwanted components. The purpose of the separation and recirculation simulation is to create a complete flow system where all the reactors are connected to each other, as would be the case in real life. Thus, the separation occurs by utilizing separation blocks (Sep blocks) for separation of by-products. An effort is also made to purify by-product streams to enable recirculation of important components such as catalysts and water. There are more purification steps present in the separation simulation than the ones stated in the block flow diagram, as some separation steps requires multiple blocks and certain components not covered in the block flow diagram must be removed to not disrupt the process downstream or to enable recirculation of components in the system.

#### 3.2.2.1 Separation and recirculation simulation using wheat bran

To make the simulation of the separation and recirculation less time-consuming, the following changes were made to the feed of raw material as well as the components in the “Properties” section to be able to simulate the separation steps in a satisfactory way.

Arabinoxylan was changed from xylose to xylan, both present in the databank containing bi-obased compounds. The reason for this is because xylan is considered a solid in the databank which makes for added simplicity when using solids separators in Aspen Plus.

In addition, some compounds were changed from conventional to solid, the purpose being to enable simpler simulation of solids separators. The current type of all compounds in the process is stated in Table 38.

Table 38. Types for the different components in the wheat bran advanced blocks separation simulation.

Compounds	Type
Protein, fat, starch, cellulose, arabinoxylan, $\beta$ -glucan, phenolic acid, ash, enzyme, heterogenic catalyst	Solid
Water, glucose, fructose, mannose, HCl, H <sub>2</sub> SO <sub>4</sub> , formic acid, levulinic acid, DMSO, DMC, HMF, arabinose, xylose	Conventional

### 3.2.2.1.1 Filter

The complete pretreatment section of the flowsheet can be seen in Figure 11.

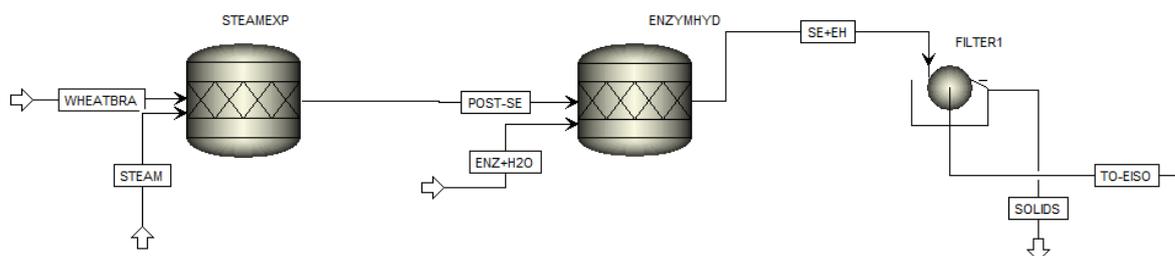


Figure 11. Overview of the pretreatment section of the flowsheet including the separation step for the advanced blocks wheat bran simulation.

After the pretreatment steps, the remaining components of wheat bran must be removed from the reaction solution together with enzymes from the enzymatic hydrolysis step. The stream exiting the pretreatment section is called *SE+EH* and has a temperature of 50°C, a pressure of 1 bar and a total mass flow of 6000 kg/h. The composition of *SE+EH* is found in Appendix B.1.2.

The *SE+EH* stream is connected to a filter block named *FILTER1* which removes the solid components from the liquid. The specifications for the filter block are found in Table 39.

Table 39. Specifications for the filtration block downstream the pretreatment reactors in the wheat bran separation simulation using advanced blocks.

Model	Solids separator
Liquid load of solid outlet	0.1
Fraction of solids to solid outlet	1
Pressure	0 bar*
Temperature change	5°C
Valid phases	Liquid-only

\* In a filter block, a pressure of 0 bar means that the pressure drop is equal to 0.

The filter results in two streams, one containing a majority of solids and one containing a majority of liquid. The liquid stream is named *TO-EISO* and is fed to the enzymatic isomerization reactor.

### 3.2.2.1.2 Removal of glucose isomerase

The isomerization section of the flowsheet can be seen in Figure 12.

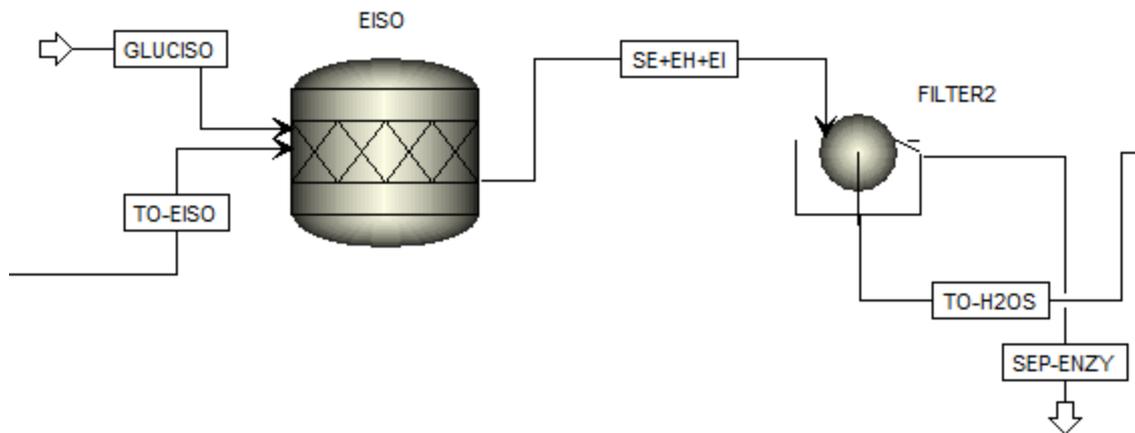


Figure 12. Overview of the isomerization section of the flowsheet including the separation step for the advanced blocks wheat bran simulation.

After the enzymatic isomerization step, the exiting flow as a total mass flow of 5349 kg/h, is 45°C and has a pressure of 1 bar. The composition of the stream can be found in Appendix B.1.2.

The glucose isomerase can be separated from the reaction mixture to enable recirculation of the enzyme back to the enzymatic hydrolysis reactor. As the enzyme is modelled as a solid (it is immobilized in reality), it is removed by the use of a filter, *FILTER2*, that separates it from the liquid fraction. The specifications for the filter can be seen in Table 40.

Table 40. Specifications for the filtration block downstream the isomerization step in the wheat bran separation simulation using advanced blocks.

Model	Solids separator
<b>Fraction of solids to solid outlet</b>	1
<b>Fraction of liquid-to-liquid outlet</b>	1
<b>Pressure</b>	1 bar
<b>Temperature</b>	45°C
<b>Valid phases</b>	Liquid-only

The outflow, now purified from glucose isomerase, is taken to the dehydration section of the process.

### 3.2.2.1.3 Removal of water

The first part of the dehydration section of the flowsheet can be seen in Figure 13.

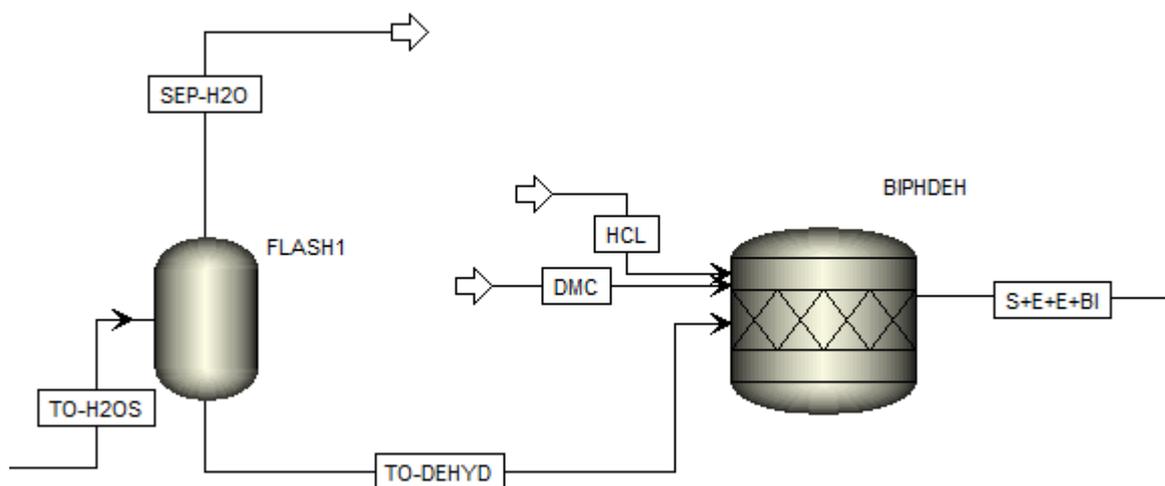


Figure 13. Overview of the first part of the dehydration section of the flowsheet including the separation step for the advanced blocks wheat bran simulation.

Before the stream can enter the biphasic dehydration reactor, the flow must have the same conditions as in the literature. This means that the concentration of fructose should be 30% fructose in water (w/v), which was obtained by the use of a Sep-block in the reactor simulation. In the separation simulation, the Sep-block is exchanged for a flash vessel. The flash vessel is modelled using the Flash2-block in Aspen. Because of the relatively small change in flow of fructose compared to the reactor simulation, when no losses of the wanted product occurred throughout the system, the calculated volume flow of the stream is assumed to be the same as the one in Appendix C. A design specification is added to specify the mass flow of water in the stream fed to the dehydration reactor, to make the flash vessel remove enough water to create the correct stream conditions. The specifications for the flash vessel *FLASH1* are found in Table 41, and the design specification is summarized in Appendix B.1.2.

Table 41. Specifications for the *FLASH1* flash vessel used in the simulation of separations for the wheat bran process using advanced blocks.

Aspen Plus Block	Flash2 <i>FLASH1</i>
Temperature	100°C
Pressure	1 bar

The outflow from the flash vessel has the correct concentration of fructose and is fed to the dehydration reactor.

### 3.2.2.1.4 Final separation

The second part of the dehydration section of the flowsheet can be seen in Figure 14.

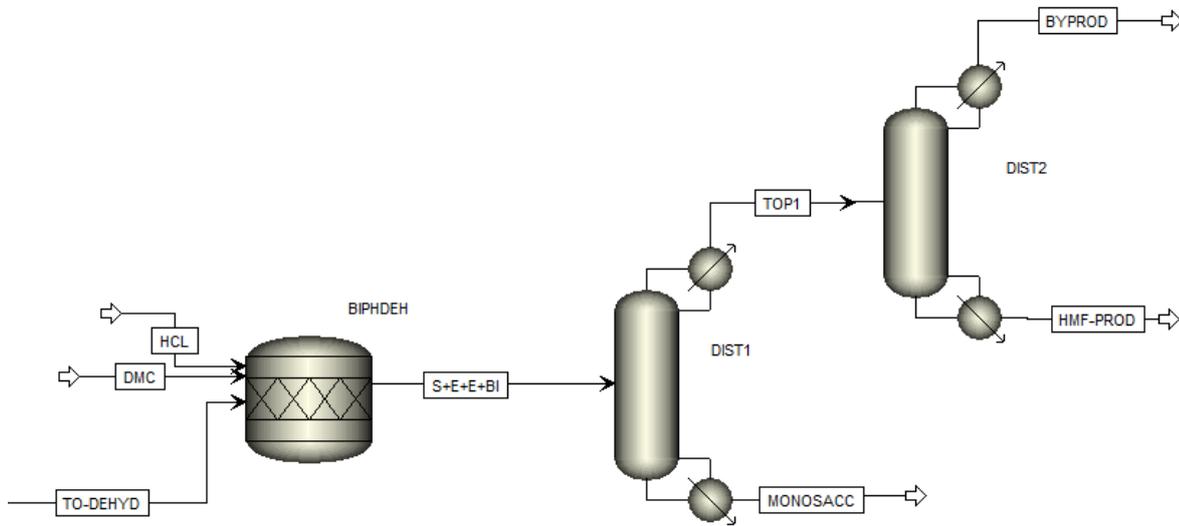


Figure 14. Overview of the second part of the dehydration section of the flowsheet including separation steps for the advanced blocks wheat bran simulation.

After the dehydration reactor, the outflowing stream  $S+E+E+BI$  has a total mass flow of 629 kg/h, is 200°C and has a pressure of 15 bar. The mass flow of the individual components is seen in Appendix B.1.2.

The goal is to produce HMF with a purity of 99 wt.%. The final separation is performed by two distillation columns,  $DIST1$  and  $DIST2$ . The specifications for the distillation columns can be seen in Table 42.

Table 42. Specifications for the  $DIST1$  and  $DIST2$  distillation columns used in the simulation of separators for the wheat bran process using advanced blocks.

Aspen Plus Block	RadFrac $DIST1$	RadFrac $DIST2$
Number of stages	11	10
Condenser	Partial-Vapor	Partial-Vapor
Reflux ratio, mass	3	3
Bottoms rate, mass	186.3 kg/h	80 kg/h
Feed streams enter on stage	6	6
Top stage condenser pressure	0.001 bar	0.001 bar

### 3.2.2.1.5 Recirculation

The complete flowsheet including separation and recirculation steps is seen in Figure 15.

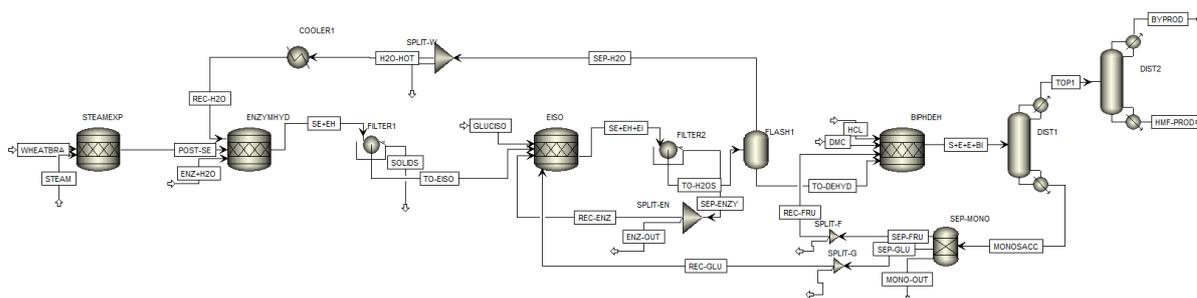


Figure 15. Overview of the entire flowsheet including separation and recirculation steps for the advanced blocks wheat bran simulation.

The glucose isomerase which was separated from the reaction mixture using *FILTER2* after the isomerization reactor is fed to a splitter which separates it to a bleed stream, *ENZ-OUT*, with 1% of the flow and a recirculation stream, *REC-ENZ*, with the remainder of the flow which is fed back to the isomerization reactor. To maintain the right amount of glucose isomerase in the system, as calculated in Appendix C, the feed of glucose isomerase is changed to 0.176 g/h.

Water was separated from the reaction mixture prior to the dehydration reactor by flashing in *FLASH1*. The separated stream has a mass flow of 4815.98 kg/h and contains 100% water. The water stream, *SEP-H2O*, is fed to a splitter which separates it to two streams called *H2O-HOT* and *H2O-OUT*. *H2O-HOT* is 4000 kg/h and is cooled to 25°C and then recycled to the enzymatic hydrolysis reactor. *H2O-OUT* contains the remainder of the flow and is used as a bleed stream. To maintain the right ratio of water in the enzymatic hydrolysis reactor, as calculated in Appendix C, the flow of water fed to the enzymatic hydrolysis is changed to 715 kg/h.

To utilize more of the monosaccharides in the system, a Sep block is placed in connection to the monosaccharide stream exiting the final separation step to resemble separation of glucose and fructose via chromatography. By using chromatography, the fructose concentration can be increased to above 90%. The sep block separates the monosaccharide stream in three streams: a fructose-rich stream, *SEP-FRU*, a glucose-rich stream, *SEP-GLU*, and a residual monosaccharide stream, *MONO-OUT*. The fructose-rich stream is fed back to the dehydration reactor, while the glucose-rich stream is fed to the isomerization reactor.

To account for the increased amount of HMF produced, the specifications of DIST1 and DIST2 are modified, as seen in Table 43.

*Table 43. Modified specifications for the DIST1 and DIST2 distillation columns used in the simulation of separators for the wheat bran process using advanced blocks.*

<b>Aspen Plus Block</b>	<b>RadFrac <i>DIST1</i></b>	<b>RadFrac <i>DIST2</i></b>
Number of stages	11	10
Condenser	Partial-Vapor	Partial-Vapor
Reflux ratio, mass	3	3
Bottoms rate, mass	438 kg/h	194 kg/h
Feed streams enter on stage	6	6
Top stage condenser pressure	0.001 bar	0.001 bar

#### 3.2.2.1.6 Assumptions for the wheat bran separation and recirculation simulation

It is assumed that the components that were changed to solid prior to the start of the separation and recirculation simulation can be simulated as solids. These components can be seen in Table 38.

It is assumed that the loss of desired components in the process is small, and therefore no amounts of for example solvents or catalysts calculated for the reactor simulation need to be changed for the separation and recirculation simulation. This assumption has been verified by calculations which can be seen in Appendix F.

### 3.2.2.2 Separation and recirculation simulation using sugar beet pulp

To make the simulation of the separation and recirculation less time-consuming, the following changes were made to the feed of raw material as well as the components in the “Properties” section to be able to simulate the separation steps in a satisfactory way.

Some compounds were changed from conventional to solid, the purpose being to enable simpler simulation of solids separators. The current type of all compounds in the process is stated in Table 44.

Table 44. Types for the different components in the sugar beet pulp advanced blocks separation simulation.

Compounds	Type
Glucan, xylan, galactan, arabinan, mannan, pectin, lignin, protein, ash, sucrose, enzyme, heterogenic catalyst	Solid
Water, glucose, fructose, mannose, arabinose, xylose, galactose, HCl, H <sub>2</sub> SO <sub>4</sub> , formic acid, levulinic acid, DMSO, DMC, HMF	Conventional

Because of changes made to the flow when some components were changed to solid, amounts of solvents and catalysts had to be changed in the reactors. The supporting calculations can be seen in Appendix G.

#### 3.2.2.2.1 Filter and sulphuric acid removal

The complete pretreatment section of the flowsheet can be seen in Figure 16.

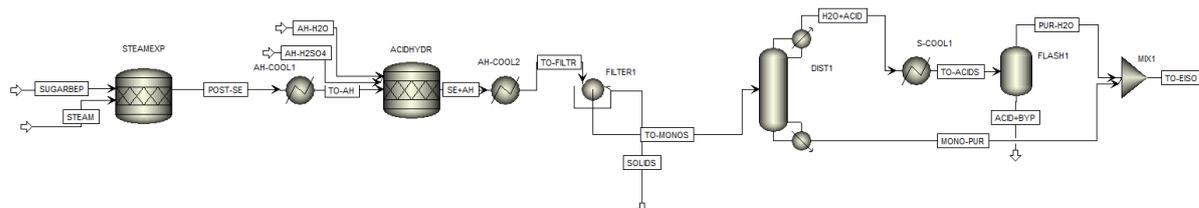


Figure 16. Overview of the pretreatment section of the flowsheet including separation steps for the advanced blocks sugar beet pulp simulation.

After the pretreatment steps, the remaining components of sugar beet pulp must be removed from the reaction solution together with the H<sub>2</sub>SO<sub>4</sub> from the acid hydrolysis step. The stream exiting the pretreatment section is called *TO-FILTR* and has a temperature of 25°C, a pressure of 1 bar and a total mass flow of 5282 kg/h. The composition of *TO-FILTR* is found in Appendix B.2.2.

The *TO-FILTR* stream is connected to a filter block named *FILTER1* which removes the solid components from the liquid. The specifications for the filter block are found in Table 45.

*Table 45. Specifications for the filtration block in the sugar beet pulp separation simulation using advanced blocks.*

<b>Model</b>	<b>Solids separator</b>
<b>Liquid load of solid outlet</b>	0.1
<b>Fraction of solids to solid outlet</b>	1
<b>Pressure</b>	0 bar*
<b>Temperature change</b>	5°C
<b>Valid phases</b>	Liquid-only

\* In a filter block, a pressure of 0 bar means that the pressure drop is equal to 0.

The filter results in two streams, one containing a majority of solids named *SOLIDS* and one containing a majority of liquid. The liquid stream, named *TO-MONOS* still contains  $H_2SO_4$  and needs to undergo additional separation. This is performed by first separating the monosaccharides from the water and  $H_2SO_4$  in a distillation column specified in Table 46.

*Table 46. Specifications for the DIST1 distillation column used in the simulation of separators for the sugar beet pulp process using advanced blocks.*

<b>Aspen Plus Block</b>	<b>RadFrac DIST1</b>
Number of stages	12
Condenser	Partial-Vapor
Reflux ratio, mass	4
Bottoms rate, mass	200 kg/h
Feed streams enter on stage	6
Top stage condenser pressure	1 bar

The distillate, which mainly contains water, H<sub>2</sub>SO<sub>4</sub> and a fraction of arabinose, is cooled down to 25°C in a heater-block and fed to a flash vessel where the H<sub>2</sub>SO<sub>4</sub> and water are separated. The specifications for the flash vessel can be seen in Table 47.

Table 47. Specifications for the FLASH1 flash vessel used in the simulation of separations for the sugar beet pulp process using advanced blocks.

Aspen Plus Block	Flash2 FLASH1
Temperature	100°C
Pressure	1 bar

The purified water exiting the flash vessel, with a mass fraction of water equal to 0.99, is mixed with the bottoms stream from the distillation column containing monosaccharides and fed to the enzymatic isomerization reactor.

### 3.2.2.2.2 Removal of glucose isomerase

The isomerization section of the flowsheet can be seen in Figure 17.

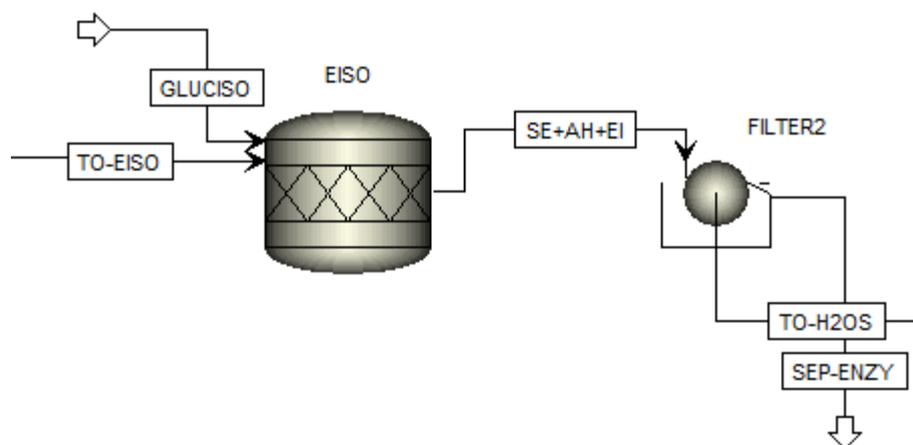


Figure 17. Overview of the isomerization section of the flowsheet including the separation step for the advanced blocks sugar beet pulp simulation.

After the enzymatic isomerization step, the exiting flow has a total mass flow of 2726 kg/h, is 45°C and a pressure of 1 bar. The composition of the stream can be seen in Appendix B.2.2.

The glucose isomerase can be separated from the reaction mixture to enable recirculation of the enzyme back to the enzymatic hydrolysis reactor. As the enzyme is modelled as a solid, it is removed by the use of a filter, *FILTER2*, that separates it from the liquid fraction. The specifications for the filter can be seen in Table 48.

Table 48. Specifications for the filtration block downstream the isomerization step in the sugar beet pulp separation simulation using advanced blocks.

Model	Solids separator
Fraction of solids to solid outlet	1
Fraction of liquid-to-liquid outlet	1
Pressure	1 bar
Temperature	45°C
Valid phases	Liquid-only

The outflow, now purified from glucose isomerase, is taken to the dehydration section of the process.

### 3.2.2.2.3 Removal of water

The first part of the dehydration section of the flowsheet can be seen in Figure 18.

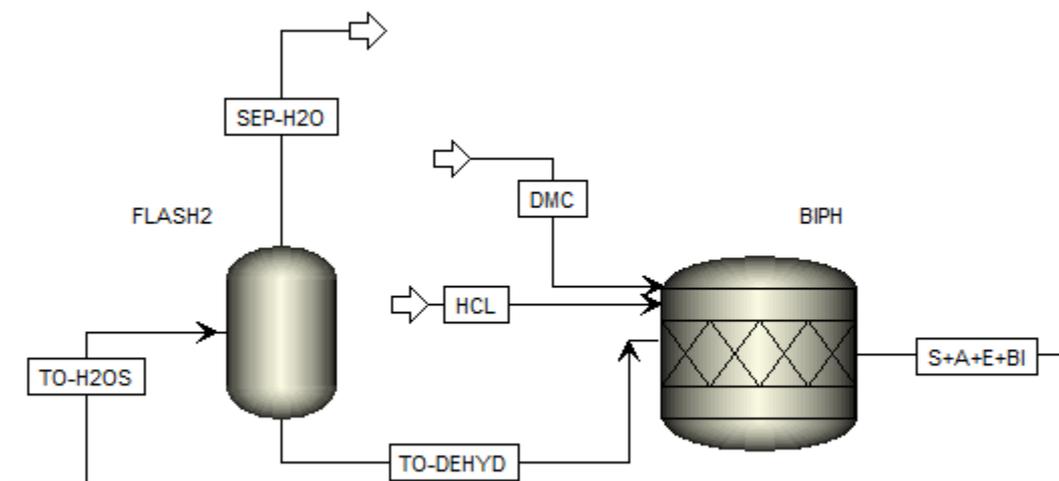


Figure 18. Overview of the first part of the dehydration section of the flowsheet including the separation step for the advanced blocks sugar beet pulp simulation.

Before the stream can enter the biphasic dehydration reactor, the flow must have the same conditions as those in the literature. This means that the concentration of fructose should be 30% fructose in water (w/v), which was obtained by the use of a Sep-block in the reactor simulation. In the separation simulation, the Sep-block is exchanged for a flash vessel. The flash vessel is modelled using the Flash2 block in Aspen. A design specification is added to specify the mass flow of water in the stream fed to the dehydration reactor, to make the flash vessel remove enough water to create the correct stream conditions. The specifications for the flash vessel *FLASH2* are found in Table 49, and the design specification is summarized in Appendix B.2.2.

Table 49. Specifications for the FLASH2 flash vessel used in the simulation of separations for the sugar beet pulp process using advanced blocks.

Aspen Plus Block	Flash2 FLASH2
Temperature	100°C
Pressure	1 bar

The outflow from the flash vessel has the correct concentration of fructose and is fed to the dehydration reactor.

### 3.2.2.2.4 Final separation

The second part of the dehydration section of the flowsheet can be seen in Figure 19.

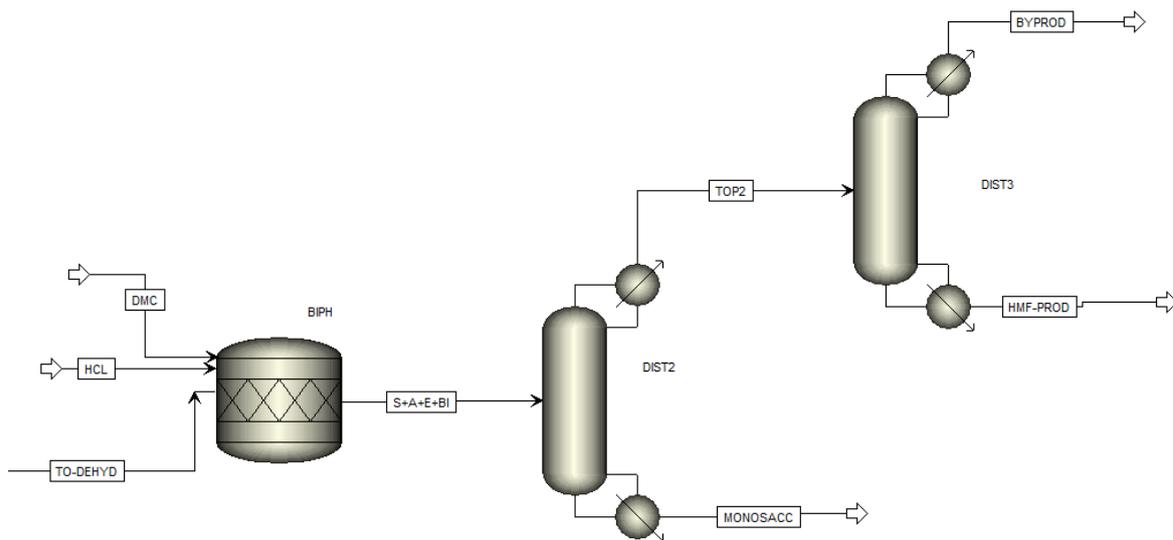


Figure 19. Overview of the second part of the dehydration section of the flowsheet including the separation step for the advanced blocks sugar beet pulp simulation.

After the dehydration reactor, the outflowing stream  $S+A+E+BI$  has a total mass flow of 274 kg/h, is 200°C and has a pressure of 15 bar. The mass flow of the individual components is seen in Appendix B.2.2.

The goal is to produce HMF with a purity of 99 wt.%. The final separation is performed by two distillation columns,  $DIST2$  and  $DIST3$ . The specifications for the distillation columns can be seen in Table 50.

Table 50. Specifications for the DIST2 and DIST3 distillation columns used in the simulation of separators for the sugar beet pulp process using advanced blocks.

Aspen Plus Block	RadFrac DIST2	RadFrac DIST3
Number of stages	20	12
Condenser	Partial-Vapor	Partial-Vapor
Reflux ratio, mass	2	5
Bottoms rate, mass	143 kg/h	33 kg/h
Feed streams enter on stage	10	2
Top stage condenser pressure	0.001 bar	0.001 bar

### 3.2.2.2.5 Recirculation

The complete flowsheet including separation and recirculation steps is seen in Figure 20.

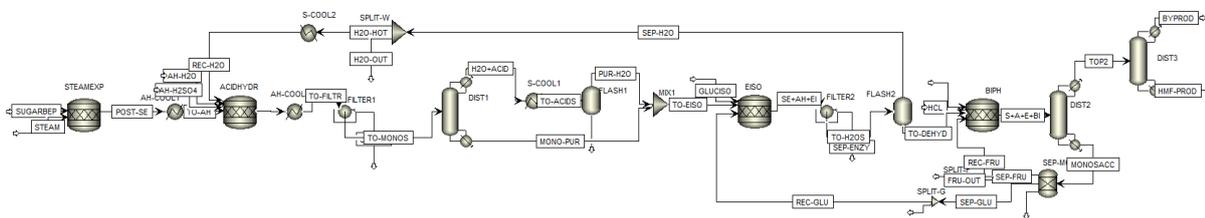


Figure 20. Overview of the entire flowsheet including separation and recirculation steps for the advanced blocks sugar beet pulp simulation.

Water was separated from the reaction mixture prior to the dehydration reactor by flashing in *FLASH2*. The separated stream has a mass flow of 2479 kg/h and contains 99.98% water. The water stream, *SEP-H2O*, is fed to a splitter which separates it to a bleed stream, two streams called *H2O-HOT* and *H2O-OUT*. *H2O-HOT* is 2000 kg/h and is cooled to 25°C and then recycled to the acid hydrolysis reactor. *H2O-OUT* contains the remainder of the flow and is used as a bleed stream. To maintain the right ratio of water in the acid hydrolysis reactor, as calculated in Appendix D, the flow of water fed to the acid hydrolysis is changed to 1956 kg/h.

To utilize more of the monosaccharides in the system, a Sep block is placed in connection to the monosaccharide stream exiting the final separation step to resemble separation of glucose and fructose via chromatography. By using chromatography, the fructose concentration can be increased to above 90%. The Sep block separates the monosaccharide stream in three streams: a fructose-rich stream, *SEP-FRU*, a glucose-rich stream, *SEP-GLU*, and a residual monosaccharide stream, *MONO-OUT*. The fructose-rich steam is fed back to the dehydration reactor, while the glucose-rich stream is fed to the isomerization reactor.

To account for the increased amount of HMF produced, the specifications of *DIST2* and *DIST3* are modified, as seen in *Table 51*.

*Table 51. Modified specifications for the DIST2 and DIST3 distillation columns used in the simulation of separators for the sugar beet pulp process using advanced blocks.*

<b>Aspen Plus Block</b>	<b>RadFrac <i>DIST2</i></b>	<b>RadFrac <i>DIST3</i></b>
Number of stages	20	12
Condenser	Partial-Vapor	Partial-Vapor
Reflux ratio, mass	2	5
Bottoms rate, mass	188.14 kg/h	61.9209 kg/h
Feed streams enter on stage	10	2
Top stage condenser pressure	0.001 bar	0.001 bar

### 3.2.2.2.6 Assumptions for the sugar beet pulp separation and recirculation simulation

It is assumed that the components that were changed to solid prior to the start of the separation and recirculation simulation can be simulated as solids. These components can be seen in *Table 44*.

### 3.2.3 Heat recovery system, utilities, and pressure changers

#### 3.2.3.1 Heat recovery system, utilities, and pressure changers simulation using wheat bran

In the previous simulations, the heater block has been used when a stream had to be cooled or heated. The aim with the heat recovery simulation is to exchange all heater blocks to HeatX blocks to enable heat exchange between streams. The aim is also to have all streams at the correct temperature before entering a block. Generally, the heat exchangers are simulated to maintain a temperature difference of minimum 8°C between the hot inlet and cold outlet steam or vice versa. The specifications of the heater block present when starting the heat recovery system simulation can be seen in Table 52. In addition, pumps need to be added in the system to enable flow of streams.

Table 52. Specifications for the heater block present in the start of the heat recovery simulations for wheat bran.

Aspen Plus Block	Heater <i>COOLER1</i>
Temperature of inlet	103°C
Temperature of outlet	25°C
Pressure of inlet and outlet	1 bar
Heat duty	-2876 kW

Heat exchangers *HEX1*, *HEX2* and *HEX3* as well as pressure changers can be seen in Figure 21 together with the temperatures of the different streams in °C.

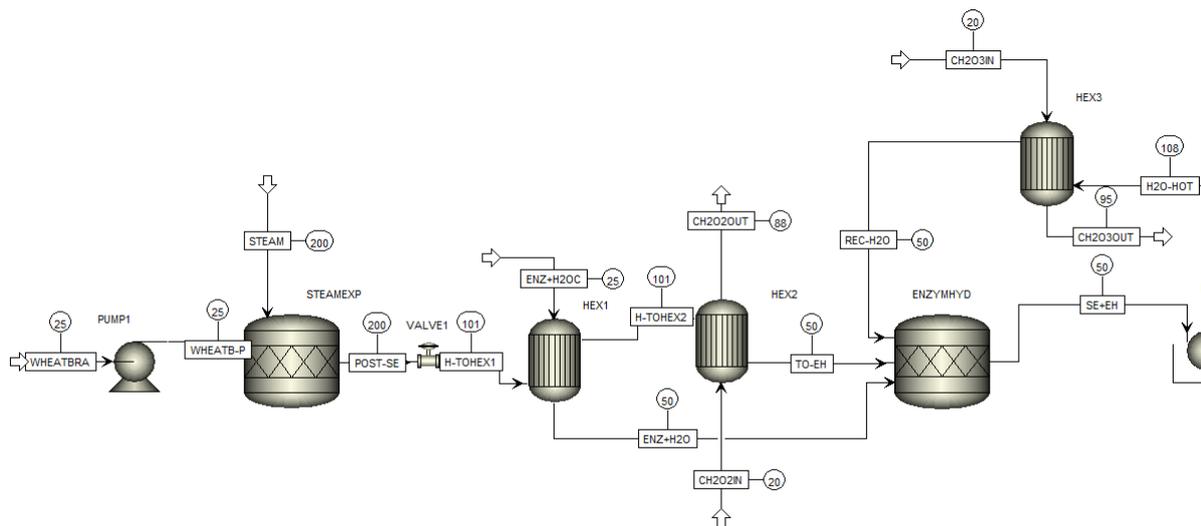


Figure 21. Heat exchangers *HEX1*, *HEX2* and *HEX3* together with pressure changers in the wheat bran simulation. The figure also includes temperatures of the streams.

A pump, *PUMPI*, is added to the wheat bran feed for it to have the same pressure as the steam, 15.51 bar. A valve, *VALVE1*, is added between the steam explosion and the enzymatic hydrolysis step to obtain the correct pressure of 1 bar for the enzymatic hydrolysis. The stream exiting the steam explosion, *H-TOHEX1*, and the combined enzyme and water stream, *ENZ+H2O*, are heat exchanged in *HEX1* for the enzyme and water stream to have the correct temperature of 50°C before entering the enzymatic hydrolysis. Subsequently, the stream exiting the steam explosion is cooled to 50°C using cooling water in *HEX2*. The same is done for the recycled water stream in *HEX3*. An overview of the three heat exchangers used for the streams entering the enzymatic hydrolysis reactor can be seen in Table 53. Specifications for the cooling water streams can be seen in Appendix B.1.3.

Table 53. Specifications of *HEX1*, *HEX2* and *HEX3* in the wheat bran advanced blocks simulation.

Aspen Plus Block	HeatX <i>HEX1</i>	HeatX <i>HEX2</i>	HeatX <i>HEX3</i>
<b>Purpose</b>	Heat <i>ENZ+H2O</i> to 50°C	Cool <i>TO-EH</i> to 50°C	Cool <i>REC-H2O</i> to 50°C
<b>Cold stream, inlet</b>	<i>ENZ+H2OC</i> at 25°C	<i>CH2O2IN</i> at 20°C	<i>CH2O3IN</i> at 20°C
<b>Hot stream, inlet</b>	<i>H-TOHEX1</i> at 101°C	<i>H-TOHEX2</i> at 101°C	<i>H2O-HOT</i> at 108°C
<b>Specification</b>	Cold stream outlet temperature of 50°C	Hot stream outlet temperature of 50°C	Hot stream outlet temperature of 50°C

Heat exchangers *HEX4*, *HEX5* and *HEX6* can be seen in Figure 22 together with the temperatures of the different streams in °C.

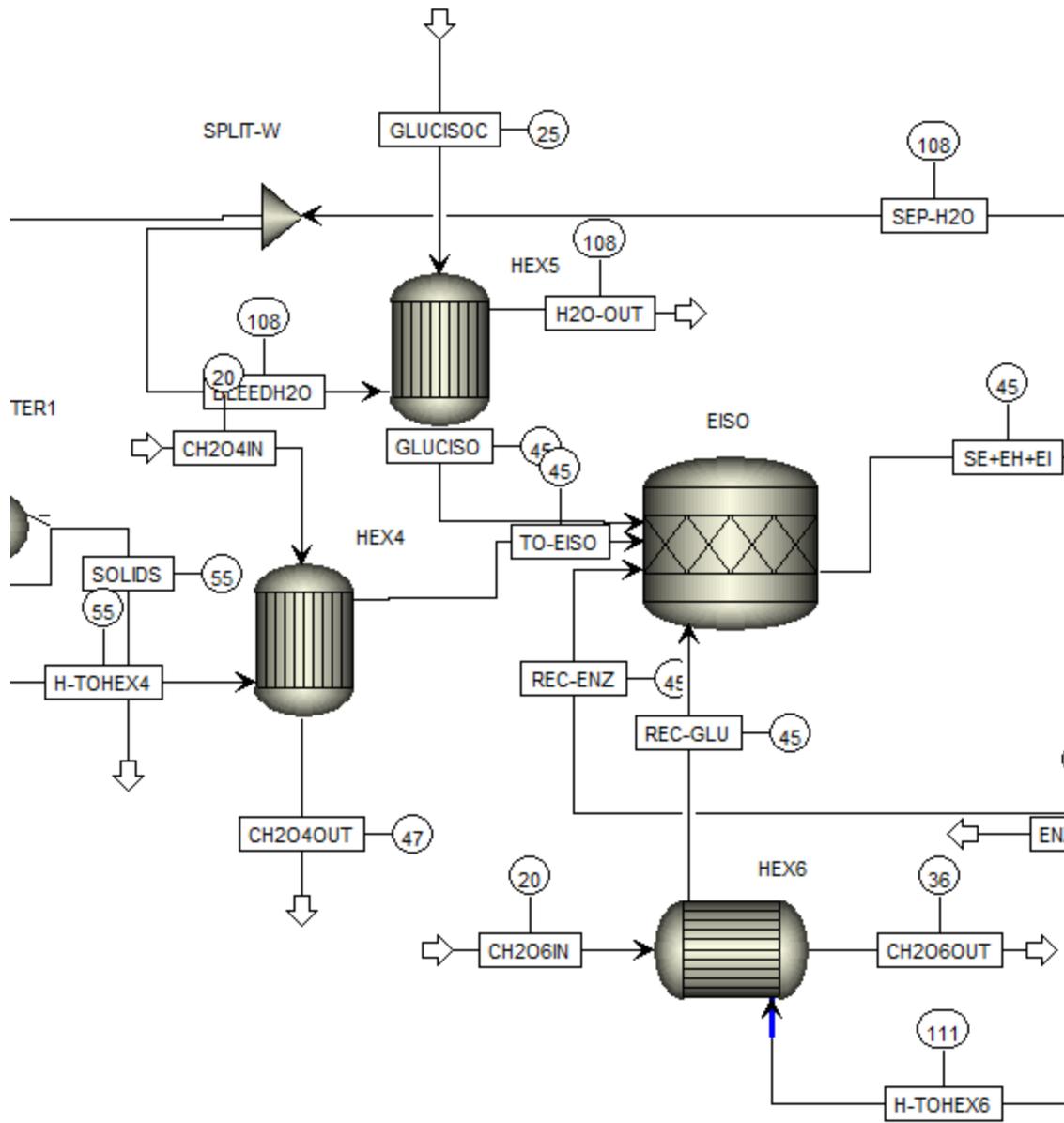


Figure 22. Heat exchangers *HEX4*, *HEX5* and *HEX6* in the wheat bran simulation including temperatures of the streams.

The reaction mixture entering the enzymatic isomerization reactor, *H-TOHEX4*, is cooled to 45°C with cooling water in *HEX4*. The glucose isomerase stream is pre-heated using the bleed stream from the water recirculation in *HEX5* before entering the enzymatic hydrolysis reactor. The recirculated glucose stream is cooled to 45°C with cooling water in *HEX6*. An overview of the heat exchangers used for the streams entering the enzymatic hydrolysis reactor can be seen in Table 54. Specifications for the cooling water streams can be seen in Appendix B.1.3.

Table 54. Specifications of HEX4 and HEX5 in the wheat bran advanced blocks simulation.

Aspen Plus Block	HeatX HEX4	HeatX HEX5	HeatX HEX6
<b>Purpose</b>	Cool TO-EISO to 45°C	Heat GLUCISO to 45°C	Cool REC-GLU to 45°C
<b>Cold stream, inlet</b>	CH2O4IN at 20°C	GLUCISOC at 25°C	CH2O6IN at 20°C
<b>Hot stream, inlet</b>	H-TOHEX4 at 55°C	BLEEDH2O at 108°C	H-TOHEX6 at 111°C
<b>Specification</b>	Hot stream outlet temperature of 45°C	Cold stream outlet temperature of 45°C	Hot stream outlet temperature of 45°C

Heat exchangers HEX7, HEX8, HEX9 and HEX10 can be seen in Figure 23 together with the temperatures of the different streams in °C.

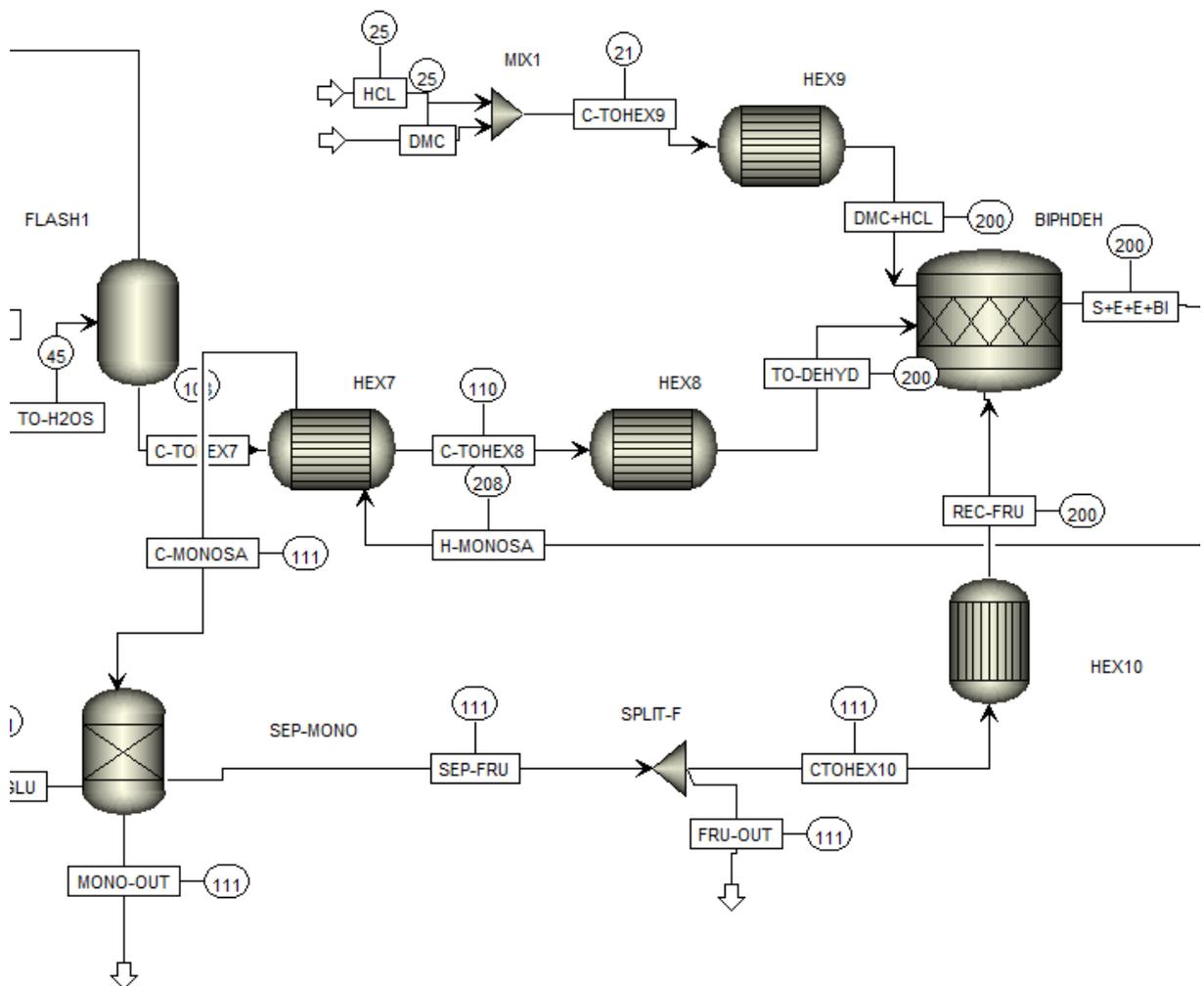


Figure 23. Heat exchangers HEX7, HEX8, HEX9 and HEX10 in the wheat bran simulation including temperatures of the streams.

The reaction mixture entering the dehydration reactor is pre-heated in two steps, firstly using the bottoms product of the first distillation tower in *HEX7* and then using the built-in utilities function in Aspen Plus in *HEX8*. The HCl and DMC-streams are mixed in *MIX1* and then pre-heated in *HEX9* using the utilities function. The recirculated fructose stream is pre-heated in *HEX10* using the utilities function. An overview of the heat exchangers used for the streams entering the dehydration reactor can be seen in Table 55. Specifications for the steam flow and the resulting mass flows calculated by Aspen Plus can be seen in Appendix B.1.3.

*Table 55. Specifications of HEX7, HEX8, HEX9 and HEX10 in the wheat bran advanced blocks simulation.*

<b>Aspen Plus Block</b>	<b>HeatX <i>HEX7</i></b>	<b>HeatX <i>HEX8</i></b>	<b>HeatX <i>HEX9</i></b>	<b>HeatX <i>HEX10</i></b>
<b>Purpose</b>	Heat <i>C-TO-HEX7</i> as much as possible	Heat <i>TO-DE-HYD</i> to 200°C	Heat <i>DMC+HCL</i> to 200°C	Heat <i>REC-FRU</i> to 200°C
<b>Cold stream, inlet</b>	<i>C-TOHEX6</i> at 108°C	<i>C-TOHEX7</i> at 110°C	<i>C-TOHEX8</i> at 21°C	<i>CTOHEX10</i> at 111°C
<b>Hot stream, inlet</b>	<i>H-MONOSA</i> at 208°C	Utility: HP-STEAM at 250°C		
<b>Specification</b>	Hot stream outlet temperature of 111°C	Cold stream outlet temperature of 200°C	Cold stream outlet temperature of 200°C	Cold stream outlet temperature of 200°C

### 3.2.3.2 Heat recovery system, utilities, and pressure changers simulation using sugar beet pulp

In the previous simulations, the heater block has been used when a stream had to be cooled or heated. The aim with the heat recovery simulation is to exchange all heater blocks to HeatX blocks to enable heat exchange between streams. The aim is also to have all streams at the correct temperature before entering a block. Generally, the heat exchangers are simulated to maintain a temperature difference of minimum 8°C between the hot inlet and cold outlet steam or vice versa. A summary of the heater blocks present in the simulation at the end of the separation and recirculation steps can be seen in Table 56. In addition, pumps need to be added in the system to enable flow of streams.

Table 56. Specifications for the heater blocks present in the start of the heat recovery simulations for sugar beet pulp.

Aspen Plus Block	<i>AH-COOL1</i>	<i>AH-COOL2</i>	<i>S-COOL1</i>	<i>S-COOL2</i>
Temperature of inlet	210°C	121°C	165°C	105°C
Temperature of outlet	25°C	25°C	25°C	25°C
Pressure of inlet and outlet	Inlet: 8 bar Outlet: 1 bar	1 bar	1 bar	1 bar
Heat duty	-522 kW	-4200 kW	-4330 kW	-1799 kW

Heat exchangers *HEX1*, *HEX2*, *HEX3*, *HEX4*, *HEX5* and *HEX6* as well as pressure changers can be seen in Figure 24 together with the temperatures of the different streams in °C.

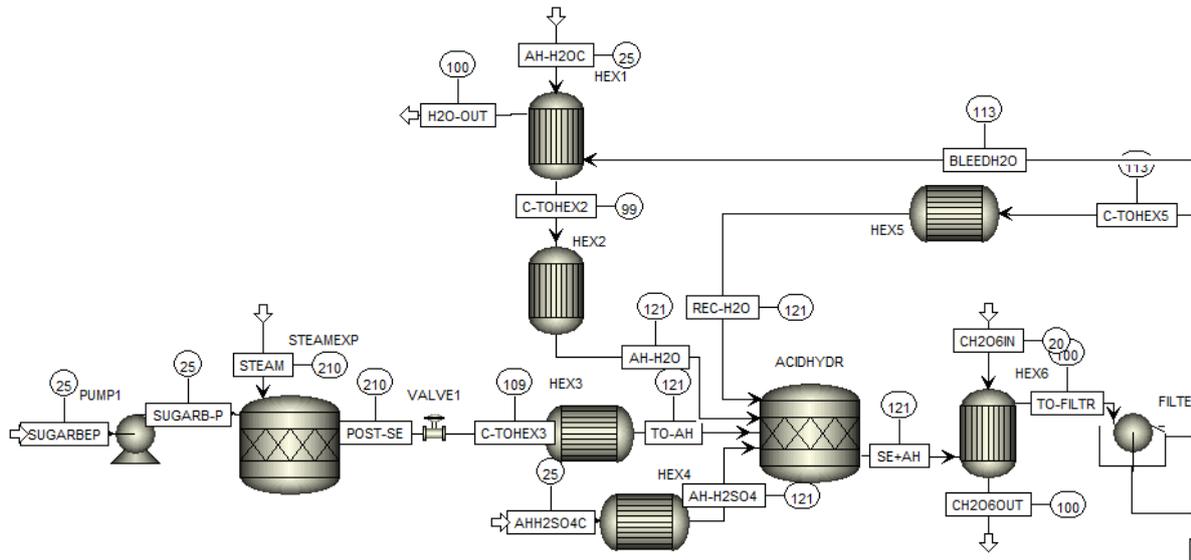


Figure 24. Heat exchangers HEX1, HEX2, HEX3, HEX4, HEX5 and HEX6 as well as pressure changers in the sugar beet pulp simulation. The figure also includes temperatures of the streams.

A pump, *PUMPI*, is added to the sugar beet pulp feed for it to have the same pressure as the steam, 19.04 bar. The water stream entering the acid hydrolysis, *AH-H2O*, is pre-heated to 121°C in two steps. In *HEX1*, the bleed stream from the water recirculation is used and in *HEX2*, the utilities function is used. A valve, *VALVE1*, is added between the steam explosion and the acid hydrolysis step to obtain the correct pressure of 1 bar for the acid hydrolysis. The valve causes the temperature of the reaction mixture to decrease below 121°C, and thus the reaction mixture is reheated in *HEX3* using the utilities function. The H<sub>2</sub>SO<sub>4</sub>-stream, *AH-H2SO4*, and the recirculated water stream, *REC-H2O*, are pre-heated using the utilities function in *HEX4* and *HEX5* respectively.

The stream exiting the acid hydrolysis step, *SE+AH*, must be cooled to have a vapor fraction equal to zero before entering *FILTER1*. This is performed in *HEX6* using cooling water. An overview of the six heat exchangers used for the streams connected to the acid hydrolysis reactor can be seen in Table 57. Specifications for the LP-steam flows as well as the specifications for the cooling water stream can be seen in Appendix B.2.3.

Table 57. Specifications of HEX1, HEX2, HEX3, HEX4, HEX5 and HEX6 in the sugar beet pulp advanced blocks simulation.

<b>Aspen Plus Block</b>	<b>HeatX HEX1</b>	<b>HeatX HEX2</b>	<b>HeatX HEX3</b>	<b>HeatX HEX4</b>	<b>HeatX HEX5</b>	<b>HeatX HEX6</b>
<b>Purpose</b>	Heat C-TO-HEX2 as much as possible	Heat AH-H2O to 121°C	Heat TO-AH to 121°C	Heat AH-H2SO4 to 121°C	Heat REC-H2O to 121°C	Cool TO-FILTR to vapor fraction = 0
<b>Cold stream inlet</b>	AH-H2OC at 25°C	C-TO-HEX2 at 99°C	C-TO-HEX3 at 109°C	AHH2SO4C at 25°C	C-TO-HEX5 at 113°C	CH2O6IN at 20°C
<b>Hot stream inlet</b>	BLEEDH2O at 113°C	Utility: LP-STEAM at 125°C				SE+AH at 121°C
<b>Specification</b>	Cold stream outlet temperature of 99°C	Cold stream outlet temperature of 121°C				Hot stream outlet vapor fraction = 0

Heat exchangers *HEX7*, *HEX8*, *HEX9* and *HEX10* can be seen in Figure 25 together with the temperatures of the different streams in °C.

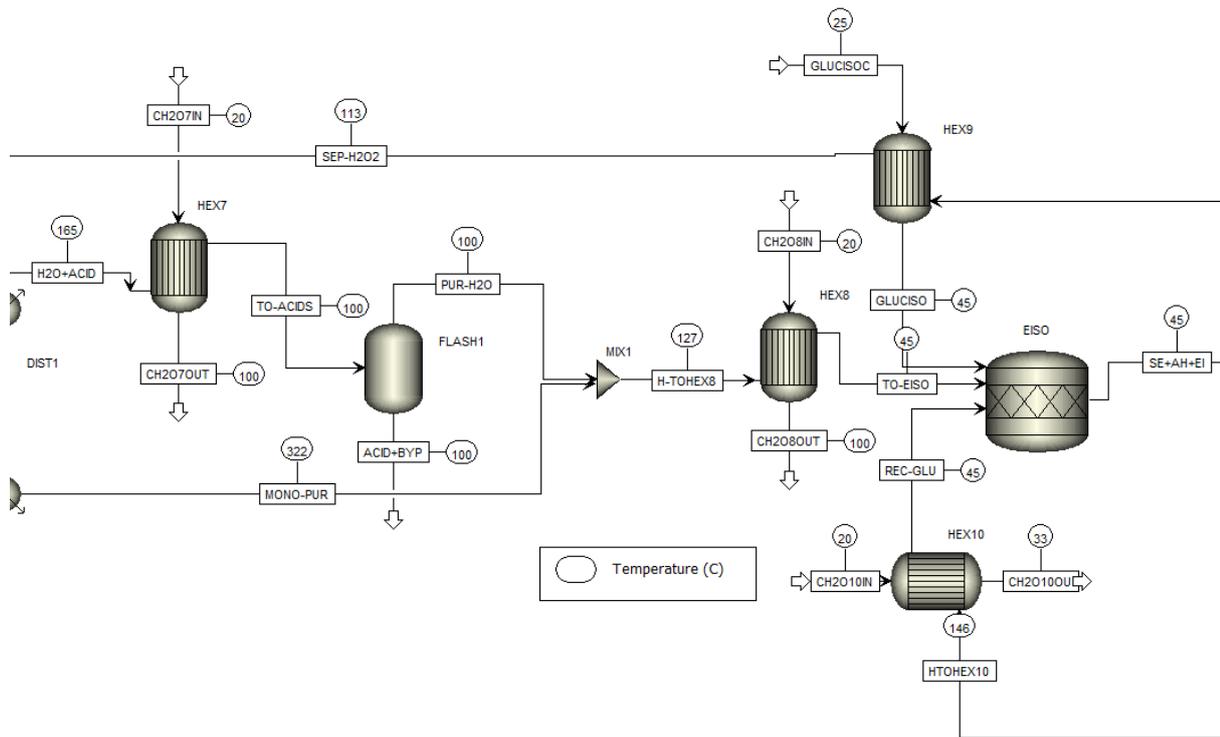


Figure 25. Heat exchangers *HEX7*, *HEX8*, *HEX9* and *HEX10* in the sugar beet pulp simulation including temperatures of the streams.

The stream exiting the first distillation tower must be cooled to have a vapor fraction equal to 0 before entering the first flash vessel. This is performed in *HEX7* with the use of a cooling water stream. In *HEX8*, the reaction mixture flowing to the enzymatic isomerization reactor is cooled to 45°C with the use of cooling water. The glucose isomerase stream to the enzymatic isomerization reactor is pre-heated to 45°C using the recirculated water stream in *HEX9*. The recirculated glucose stream is cooled to 45°C using cooling water in *HEX10*. An overview of the four heat exchangers used in connection to the enzymatic isomerization reactor and the H<sub>2</sub>SO<sub>4</sub> separation reactor can be seen in Table 58. The specifications for the cooling water streams can be seen in Appendix B.2.3.

Table 58. Specifications of HEX7, HEX8, HEX9 and HEX10 in the sugar beet pulp advanced blocks simulation.

Aspen Plus Block	HeatX HEX7	HeatX HEX8	HeatX HEX9	HeatX HEX10
<b>Purpose</b>	Cool <i>TO-ACIDS</i> to vapor fraction = 0	Cool <i>TO-EISO</i> to 45°C	Heat <i>GLUCISO</i> to 45°C	Cool <i>REC-GLU</i> to 45°C
<b>Cold stream inlet</b>	<i>CH2O7IN</i> at 20°C	<i>CH2O8IN</i> at 20°C	<i>GLUCISOC</i> at 25°C	<i>CH2O10IN</i> at 20°C
<b>Hot stream inlet</b>	<i>H2O+ACID</i> at 164.982°C	<i>H-TOHEX8</i> at 126.815°C	<i>SEP-H2O1</i> at 112.967°C	<i>HTOHEX10</i> at 145.69°C
<b>Specification</b>	Hot stream outlet vapor fraction = 0	Hot stream outlet temperature of 45°C	Cold stream outlet temperature of 45°C	Hot stream outlet temperature of 45°C

Heat exchangers *HEX11*, *HEX12* and *HEX13* can be seen in Figure 26 together with the temperature of the different streams in °C.

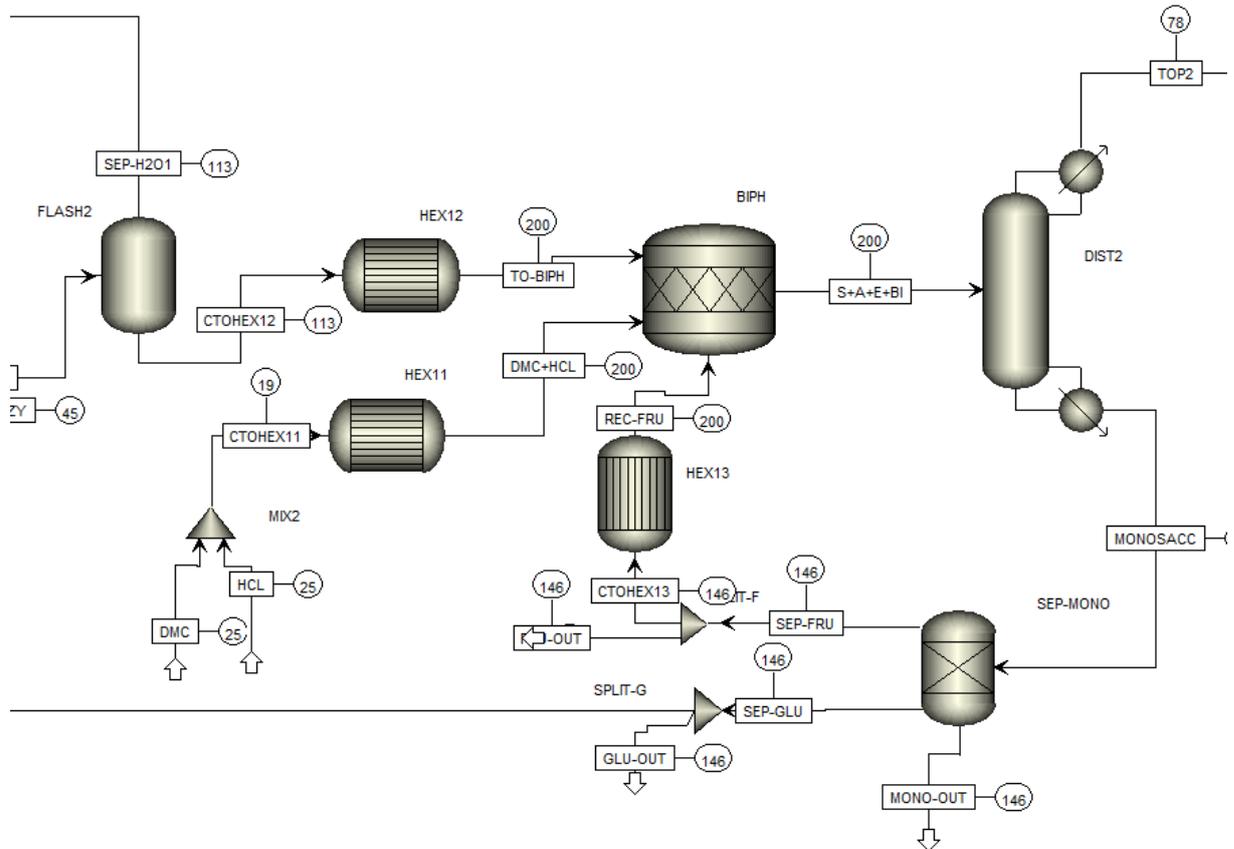


Figure 26. Heat exchangers *HEX11*, *HEX12* and *HEX13* in the sugar beet pulp simulation including temperatures of the streams.

The DMC- and HCl-streams are mixed and pre-heated to 200°C using the utilities function in *HEX11*, while the reaction mixture is pre-heated in *HEX12*, also using the utilities function. In *HEX13*, the recirculated fructose-stream is pre-heated to 200°C using the utilities function. An overview of the three heat exchangers used for the streams connected to the dehydration reactor can be seen in

Table 59, while the specifications for the HP-steam flows can be seen in Appendix B.2.3.

*Table 59. Specifications of HEX10 and HEX11 in the sugar beet pulp advanced blocks simulation.*

<b>Aspen Plus Block</b>	<b>HeatX <i>HEX11</i></b>	<b>HeatX <i>HEX12</i></b>	<b>HeatX <i>HEX13</i></b>
<b>Purpose</b>	Heat <i>DMC+HCL</i> to 200°C	Heat <i>TO-BIPH</i> to 200°C	Heat <i>REC-FRU</i> to 200°C
<b>Cold stream, inlet</b>	<i>CTOHEX11</i> at 19.3357°C	<i>CTOHEX12</i> at 112.967°C	<i>CTOHEX13</i> at 112.967°C
<b>Hot stream, inlet</b>	Utility: HP-STEAM at 250°C		
<b>Specification</b>	Cold stream outlet temperature of 200°C		

## 4 Economic evaluation

To evaluate the processes economically, an indicator called *Metric for Inspecting Sales and Reactants*, shortened MISR, is used. The formula for calculating MISR can be seen in Equation 1. A high MISR value is desirable, and a value above 1 means that the process can be considered for further analysis.<sup>57</sup>

$$MISR = \frac{\sum_{p=1}^{N_{Products}} \text{Annual production rate of product } p \cdot \text{Selling price of product } p}{\sum_{r=1}^{N_{Reactants}} \text{Annual feed rate of reactant } r \cdot \text{Purchased price of reactant } r} \quad (1)$$

Two scenarios were analysed for both raw materials, the first being varying the selling price of HMF and the second being varying the purchased price of the raw material. For both scenarios, it is assumed that the process is in steady state. No cost of cooling water, steam or process water is included.

In the first scenario, the following was assumed for wheat bran:

A production period of 8000 production hours per year, hourly production rate of 79.9798 kg HMF before recirculation of monosaccharides and 193.842 kg HMF after recirculation of monosaccharides. The hourly feed rate of raw material is 1000 kg, the price of wheat bran was 9.05 SEK/kg if bought in sacks<sup>58</sup>. The price could be cheaper if the plant is located near a wheat bran producer such as a mill, which lowers cost of transportation. The hourly feed rate of the remaining reactants is: 0.178 kg amyloglucosidase/h, 0.000176 kg glucose isomerase/h, 78.3 kg DMC/h and 17.3181 kg HCl/h. The prices used are as follows: \$25/kg amyloglucosidase<sup>59</sup>, \$100/kg glucose isomerase<sup>60</sup>, \$10/kg DMC<sup>61</sup> and \$125/ton HCl<sup>62</sup>. The exchange rate used is 1 USD = 8.3903 SEK<sup>63</sup>.

The following was assumed for sugar beet pulp:

A production period of 8000 production hours per year, hourly production rate of 32.6108 kg HMF before recirculation of monosaccharides and 56.2781 kg HMF after recirculation of monosaccharides. The hourly feed rate of raw material is 1000 kg, and the price of sugar beet pulp was 109 SEK for 15 kg<sup>64</sup>. The price could be cheaper if the plant is located near a sugar producer, such as a sugar refinery, which lowers cost of transportation. The hourly feed rate of the remaining reactants is: 41.4537 kg H<sub>2</sub>SO<sub>4</sub>/h, 0.003 kg glucose isomerase/h, 17.8 kg DMC/h and 6.75 kg HCl/h. The prices used are as follows: \$200/ton H<sub>2</sub>SO<sub>4</sub><sup>65</sup>, \$100/kg glucose isomerase<sup>60</sup>, \$10/kg DMC<sup>61</sup> and \$125/ton HCl<sup>62</sup>. The exchange rate used is 1 USD = 8.3903 SEK<sup>63</sup>.

The resulting charts can be seen in Figure 27 and Figure 28.

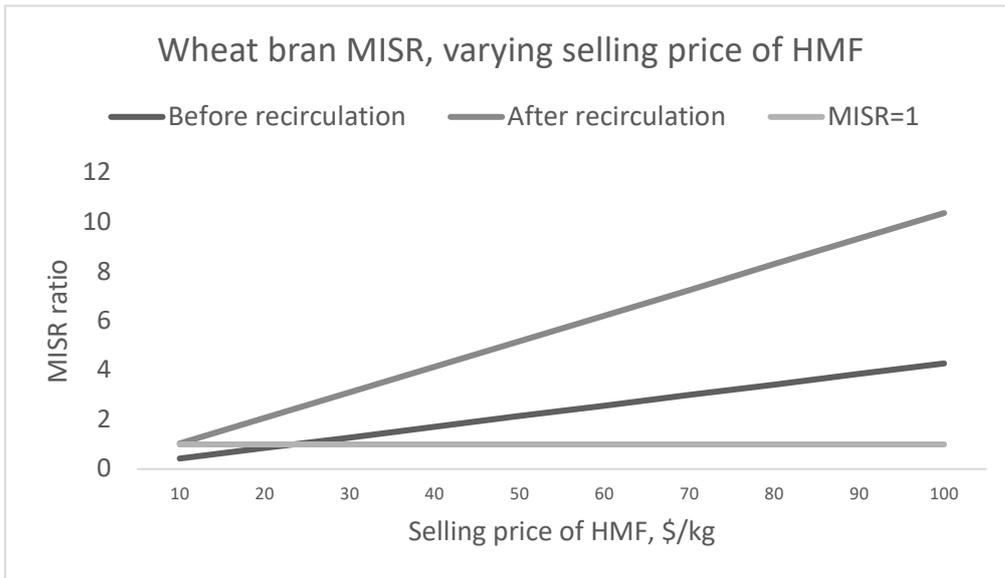


Figure 27. MISR chart for wheat bran with varying selling prices of HMF.

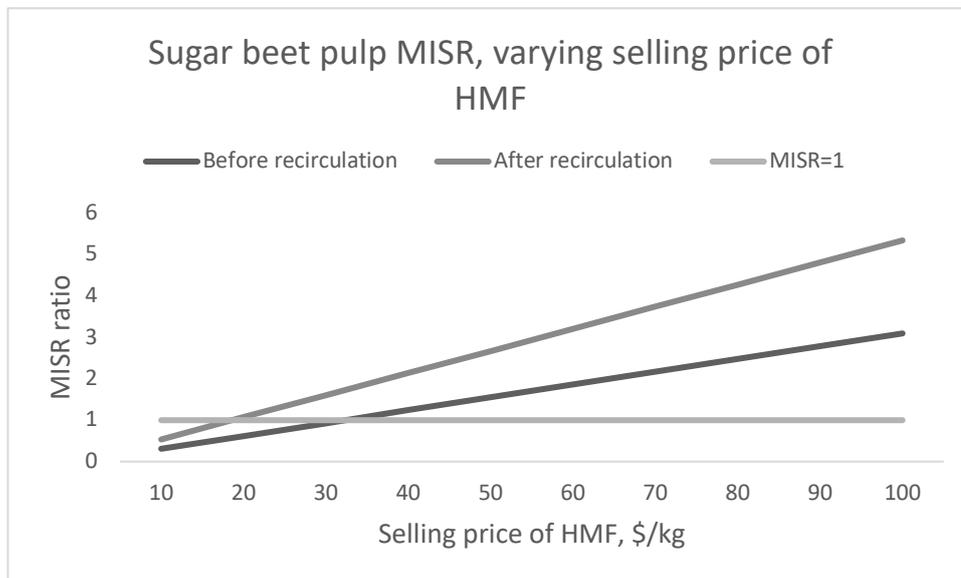


Figure 28. MISR chart for sugar beet pulp with varying selling prices of HMF.

In the second scenario, the following was assumed for wheat bran:

A production period of 8000 production hours per year, hourly production rate of 79.9798 kg HMF before recirculation of monosaccharides and 193.842 kg HMF after recirculation of monosaccharides. The selling price of HMF was \$240 per kg<sup>10</sup>. The hourly feed rate of raw material is 1000 kg. The hourly feed rate of the remaining reactants is: 0.178 kg amyloglucosidase/h, 0.000176 kg glucose isomerase/h, 78.3 kg DMC/h and 17.3181 kg HCl/h. The prices used are as follows: \$25/kg amyloglucosidase<sup>59</sup>, \$100/kg glucose isomerase<sup>60</sup>, \$10/kg DMC<sup>61</sup> and \$125/ton HCl<sup>62</sup>. The exchange rate used is 1 USD = 8.3903 SEK<sup>63</sup>.

The following was assumed for sugar beet pulp:

A production period of 8000 production hours per year, hourly production rate of 32.6108 kg HMF before recirculation of monosaccharides and 56.2781 kg HMF after recirculation of monosaccharides. The selling price of HMF was \$240 per kg<sup>10</sup>. The hourly feed rate of raw material is 1000 kg. The hourly feed rate of the remaining reactants is: 41.4537 kg H<sub>2</sub>SO<sub>4</sub>/h, 0.003 kg glucose isomerase/h, 17.8 kg DMC/h and 6.75 kg HCl/h. The prices used are as follows: \$200/ton H<sub>2</sub>SO<sub>4</sub><sup>65</sup>, \$100/kg glucose isomerase<sup>60</sup>, \$10/kg DMC<sup>61</sup> and \$125/ton HCl<sup>62</sup>. The exchange rate used is 1 USD = 8.3903 SEK<sup>63</sup>.

The resulting charts can be seen in Figure 29 and Figure 30.

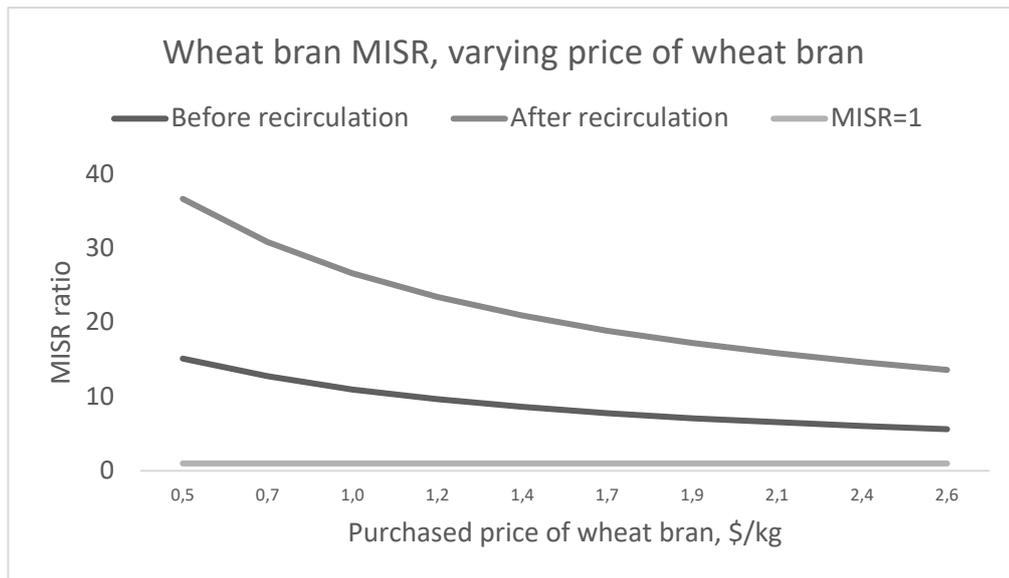


Figure 29. MISR chart for wheat bran with varying prices of wheat bran.

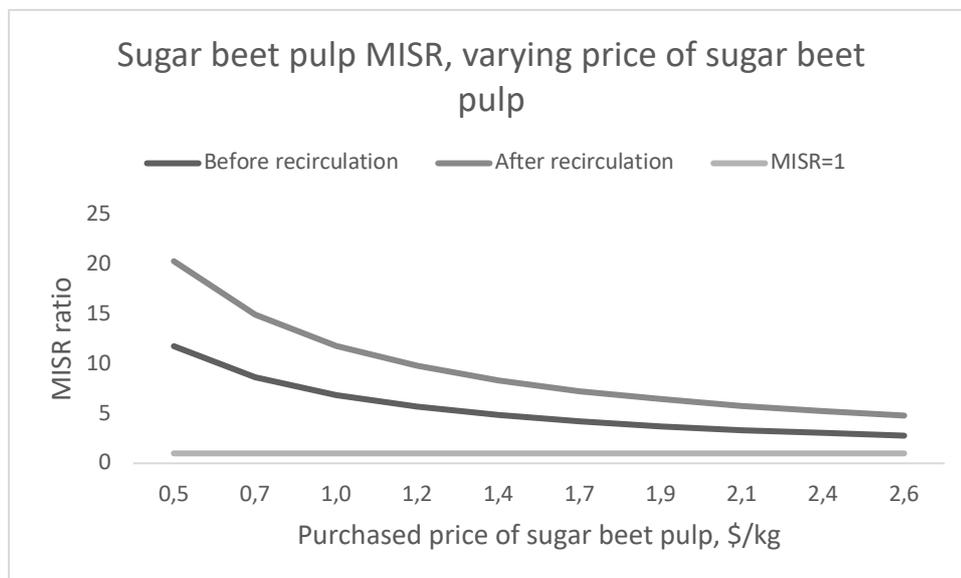


Figure 30. MISR chart for sugar beet pulp with varying prices of sugar beet pulp.



# 5 Results and discussion

## 5.1 Results of the process simulation

The results of the simulations using simple blocks are shown in Table 60. For the simple block simulations, a raw material flow of 100 kg/h was used.

Table 60. Summary of the resulting HMF-stream in the simple block simulation.

Raw material	Wheat bran	Sugar beet pulp
Mass flow of product stream	11.32 kg/h	7.451 kg/h
Mass purity of HMF in product stream	100%	100%

The complete flowsheet showing the reactor simulation can be seen in Figure 31. The flowsheet looks similar for both wheat bran and sugar beet pulp and includes all options for the different reactor steps. The reactor simulation results in 12 different outflows for the two raw materials respectively, representing the different reactor combinations.

In Appendix E, a comparison of the twelve different reactor combinations can be seen. The table in Appendix E was used to decide which combination of reactors to use for the continued simulations.

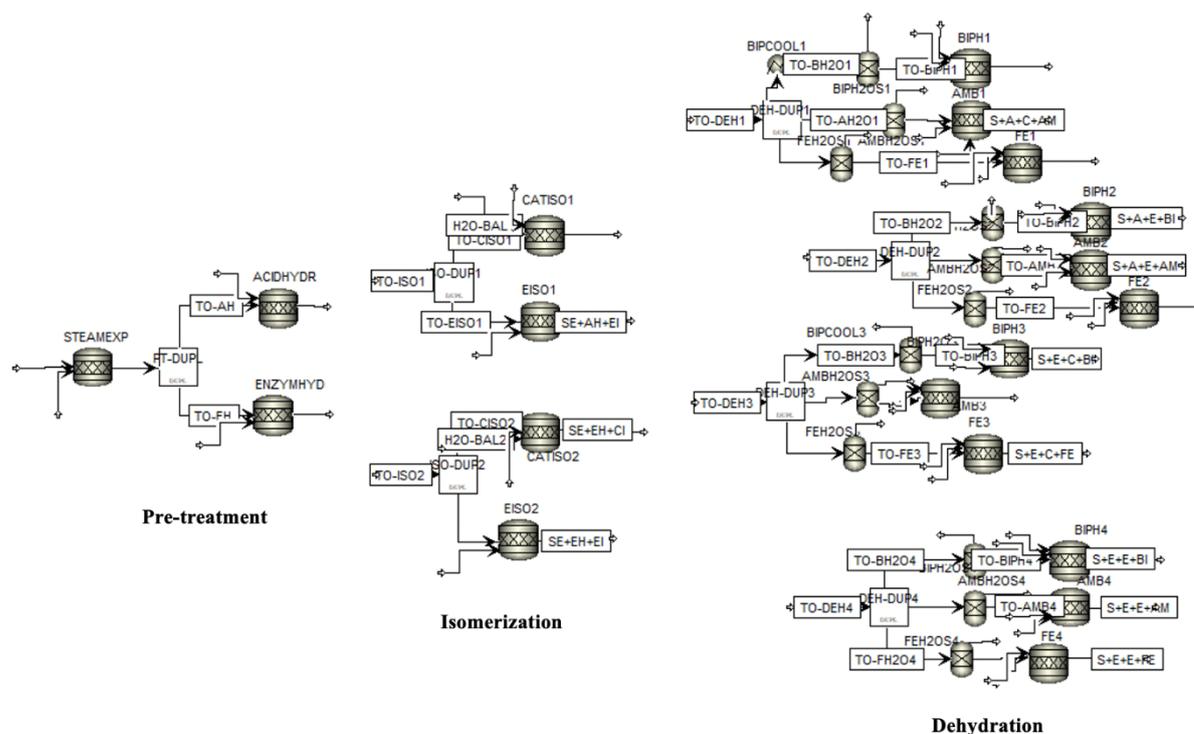


Figure 31. The complete flowsheet for the advanced blocks reactor simulation with the three sections marked. The layout of the flowsheet is the same for the two raw materials.



In Table 61 and Table 62, a summary of the separation and recirculation simulations can be seen for both raw materials before and after recirculation of streams.

*Table 61. Summary of the results of the separation and recirculation simulation for wheat bran before and after implementation of recirculation streams.*

<b>Raw material</b>	<b>Wheat bran, before recirculation of monosaccharides</b>	<b>Wheat bran, after recirculation of monosaccharides</b>
<b>Mass flow of product stream</b>	80.0 kg/h	194 kg/h
<b>Mass purity of HMF in product stream</b>	100%	100%

*Table 62. Summary of the results of the separation and recirculation simulation for sugar beet pulp before and after implementation of recirculation streams.*

<b>Raw material</b>	<b>Sugar beet pulp, before recirculation of monosaccharides</b>	<b>Sugar beet pulp, after recirculation of monosaccharides</b>
<b>Mass flow of product stream</b>	33 kg/h	58 kg/h
<b>Mass purity of HMF in product stream</b>	98.8%	96.7%

The resulting flowsheets of the heat exchanger, utilities and pressure changers simulation can be seen in Figure 34 for wheat bran and in Figure 35 for sugar beet pulp.

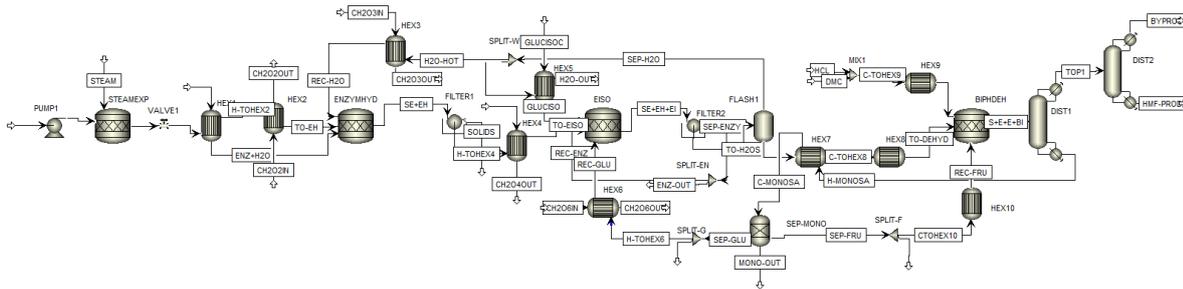


Figure 34. The complete flowsheet for the heat exchangers, utilities, and pressure changers simulation with wheat bran as raw material.

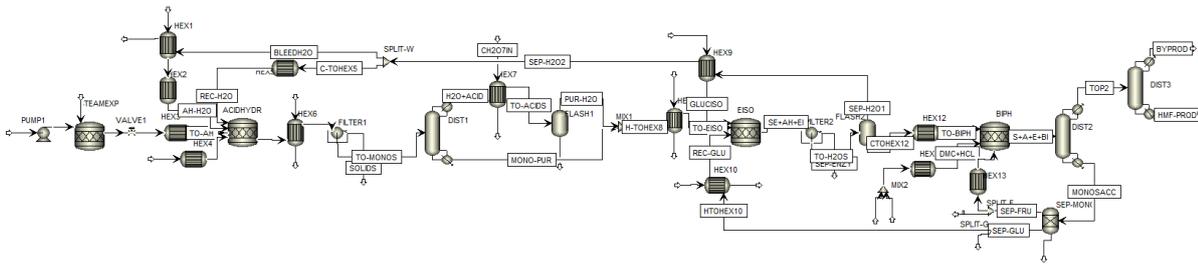


Figure 35. The complete flowsheet for the heat exchangers, utilities, and pressure changers simulation with sugar beet pulp as raw material.

In Figure 36 and Figure 37, the complete flowsheets for the wheat bran and sugar beet pulp simulations are shown including colorized flow paths for different categories of components. The different colors represent the following: light green = valuables, red = by-products, dark blue = steam, yellow = catalyst and solvent, light blue = cooling water, mid-blue = recirculated water and pure water streams, dark green = recycled reactant.

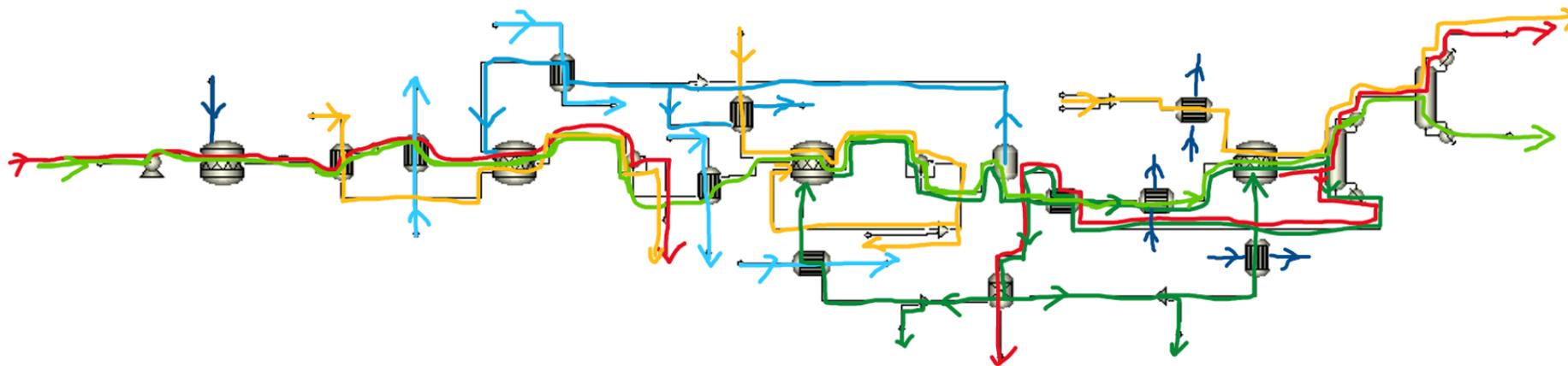
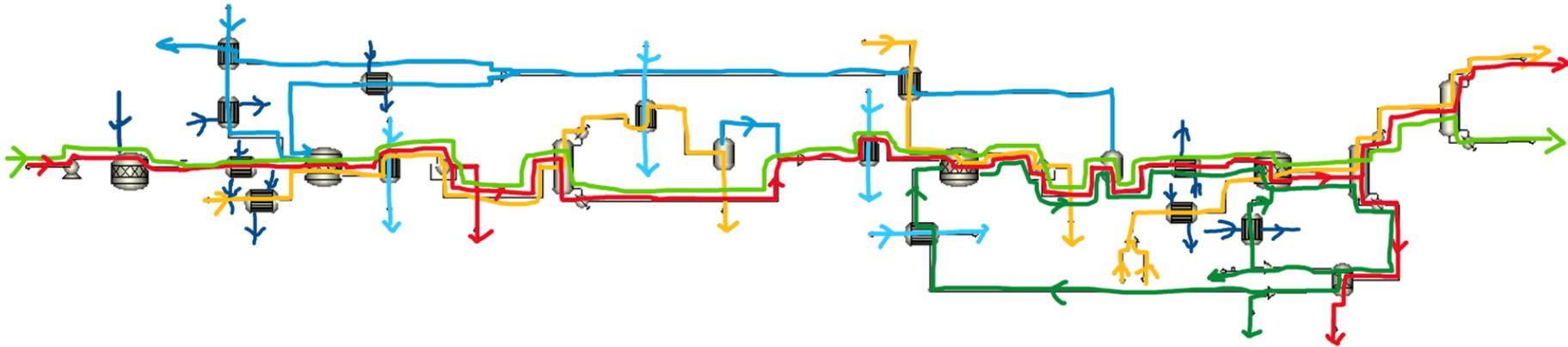


Figure 36. The complete flowsheet for the heat exchangers, utilities, and pressure changers simulation with wheat bran as raw material, including colorized flow paths for different categories of components. The different colors represent the following: light green = valuables, red = by-products, dark blue = steam, yellow = catalyst and solvent, light blue = cooling water, mid-blue = recirculated water and pure water streams, dark green = recycled reactant.



*Figure 37. The complete flowsheet for the heat exchangers, utilities, and pressure changers simulation with sugar beet pulp as raw material, including colorized flow paths for different categories of components. The different colors represent the following: light green = valuables, red = byproducts, dark blue = steam, yellow = catalyst and solvent, light blue = cooling water, mid-blue = recirculated water and pure water streams, dark green = recycled reactant.*

In Table 63, Table 64 and Table 65, the theoretical yields as well as yields before and after implementation of recirculation of monosaccharides can be seen for both feedstocks.

*Table 63. Theoretical yield of HMF from the different raw materials. The supporting calculations can be seen in Appendix H.*

<b>Raw material</b>	<b>Wheat bran</b>	<b>Sugar beet pulp</b>
Yield of HMF from dry weight [wt.%]	29.8%	17.7%
Yield of HMF from the reacting fraction of the dry weight [wt.%]	77.7%	77.3%

*Table 64. Yield of HMF from the different raw materials in the finalized process simulation without recirculation of monosaccharides. The supporting calculations can be seen in Appendix I.*

<b>Raw material</b>	<b>Wheat bran</b>	<b>Sugar beet pulp</b>
Yield of HMF from dry weight [wt.%]	8.0%	3.3%
Yield of HMF from the reacting fraction of the dry weight [wt.%]	20.8%	14.2%

*Table 65. Yield of HMF from the different raw materials in the finalized process simulation including recirculation of monosaccharides. The supporting calculations can be seen in Appendix I.*

<b>Raw material</b>	<b>Wheat bran</b>	<b>Sugar beet pulp</b>
Yield of HMF from dry weight [wt.%]	19.4%	5.6%
Yield of HMF from the reacting fraction of the dry weight [wt.%]	50.5%	24.6%

## 5.2 Discussion

Throughout the simulations, several observations could be made regarding the differences between the requirements for the two different raw materials. A visualization of the performance of the different reactor step combinations can be seen in Appendix E.

In the pretreatment step for wheat bran, the use of an enzymatic hydrolysis step resulted in a higher amount of extracted glucose than an acid hydrolysis step. The enzymes were also more specific, yielding smaller amounts of by-products. The use of enzymatic hydrolysis resulted in more than 40 kg additional fructose per hour after isomerization for both the steam explosion, enzymatic hydrolysis and chemical or enzymatic isomerization respectively, compared to their respective counterparts using acid hydrolysis.

In the pretreatment step for sugar beet pulp, acid hydrolysis with  $\text{H}_2\text{SO}_4$  proved to be superior to its enzymatic counterpart due to the ability of the acid hydrolysis to extract additional fructose. The use of acid hydrolysis resulted in more than 30 kg additional fructose per hour after isomerization for both the steam explosion, acid hydrolysis and chemical or enzymatic isomerization respectively, compared to their respective counterparts using enzymatic hydrolysis. For simplicity, the formed fructose was assumed not to affect the equilibrium in the isomerization step, which would not be the case in real life settings. The amount of fructose formed would probably be lower, and this would need to be investigated further by additional experiments.

For both raw materials, enzymatic isomerization using glucose isomerase proved to be more effective for conversion from glucose to fructose than chemical isomerization using  $\text{Sn-}\beta$  catalyst. This is due to the specificity of glucose isomerase, which also has the added benefit of an equilibrium concentration at 48% fructose, while the equilibrium for  $\text{Sn-}\beta$  is at 31% fructose. Use of  $\text{Sn-}\beta$  as catalyst for the isomerization step also means additional by-product formation in the form of mannose. Enzymatic isomerization resulted in more than 19 and 7 kg additional fructose formed per hour for wheat bran and sugar beet pulp, respectively, compared to chemical catalyst isomerization.

For both raw materials, dehydration using Amberlyst 15 powder produced the most HMF compared to the  $\text{FePW}_{12}\text{O}_{40}$  catalyst and the  $\text{HCl/DMC}$  system. However, due to the use of DMSO as the solvent which is connected to separation problems after the reactor as well as environmental concerns, the  $\text{HCl/DMC}$  system was chosen instead. Choosing the Amberlyst 15 powder had resulted in 3-11 additional kilograms of HMF per hour, but in turn would cause other problems related to environmental concerns and difficulty in separation.

The choices of reactor steps highly affect the type and extent of separation equipment needed, which can clearly be seen in the separation and recirculation simulation. The wheat bran simulation, which does not include any pretreatment steps involving any acid, demands less separation between the pretreatment and isomerization step than does the sugar beet pulp simulation, in which acid hydrolysis is performed. In comparison, the wheat bran simulation contains a filter for removal of residual solids between the pretreatment and isomerization steps, while the sugar beet pulp simulation includes a filter, a distillation column, and a flash vessel together with two heaters and a mixer to remove residual solids and acid.

It is safe to assume that if a calculation of the investment costs of the two processes would have been made, it would have resulted in a higher investment cost for the sugar beet pulp process because of its additional equipment.

When deciding which streams were to be recirculated, two criteria were set up to make the process simpler. The first criterion was that the stream could not contain a too large variety of components, because that would complicate the separation process and thus add additional equipment. The second criterion was that the stream would need to be of sufficient size to assure that there is a benefit from the recirculation. From the criteria, a few streams were ruled out. The solids stream for both raw materials contained too many different components which also behaved similarly, which overcomplicated the separation process. This was also the case for the *BYPROD* stream in the wheat bran simulation as well as the *BYPROD* and *ACID+BYP* streams in the sugar beet pulp simulation. The glucose isomerase stream was recirculated in the wheat bran simulation but not in the sugar beet pulp simulation, as it caused problems in Aspen Plus due to its relatively small size. The small size of the stream is due to a very small mass of enzyme is needed for conversion, only 3 g/h in total.

An important aspect when designing the final separation after the dehydration reactor is the thermal stability of HMF. HMF decomposes at temperatures above 130°C, which is important to take into consideration. Because of this property, distillation might not be optimal choice of separation process for the final purification step in real-life settings. Another limiting factor of distillation is that the pressure in the distillation columns used for the final separation of HMF in both the wheat bran and sugar beet pulp simulation is only 1 mbar, which makes it technically challenging. Thus, obtaining this pressure in reality is, of course, more complicated than in Aspen Plus. If a pilot plant is to be built, distillation should be compared to other possible separation processes. An example of another suitable separation process is evaporation, which was used successfully on the HCl/DMC-system by Sayed et. al.

The difference between the combination of reactor steps also becomes evident in the heat exchangers, utilities, and pressure changers simulation, where the wheat bran simulation includes a total of 10 heat exchangers whereas the sugar beet pulp simulation includes 13. An explanation for this can be the temperatures in the system. The wheat bran simulation includes enzymatic hydrolysis and isomerization, which take place at lower temperatures than the acid hydrolysis used for production from sugar beet pulp. This is also stated in section 3.2.1.3.1 Processes which will be used in further simulations – Wheat bran: “The enzymatic conversion steps also have the added benefit of fewer by-products and lower temperatures, which can affect the energy used for heating the system”. An interesting point would be to compare the amount of unit operations needed in the two present simulations to a wheat bran simulation, which includes acid hydrolysis and a sugar beet pulp simulation, which includes enzymatic hydrolysis.

As expected, none of the raw materials were able to obtain the theoretical yield, which is due to the utilization rate of the reacting fraction being lower than 100%. In addition, the simulation does not include reaction kinetics which will highly affect the produced amount of HMF.

When recirculating the monosaccharides from the final separation step in the wheat bran process, the yield of HMF from the reacting fraction of the dry weight rose from 20.8% to 50.5%, compared to the theoretical yield of 77.7%. Similarly, implementing the recirculation of monosaccharides improved the yield of HMF from the reacting fraction of the dried sugar beet pulp rose from 14.2% to 24.6%, compared to the theoretical yield of 77.3%. The reacting fraction of wheat bran is larger than the reacting fraction of sugar beet pulp, which of course affects the amount of HMF formed. When comparing the obtained yields from the entire wheat bran to the ones obtained in the process, the theoretical yield of HMF from wheat bran was 29.8% while the obtained yields were 8.0% and 19.4% before and after recirculation respectively. For sugar beet pulp, the theoretical yield was 17.7% while the obtained yields of HMF were 3.3% and 5.6% respectively. It is evident that the wheat bran process performs better in terms of yield than the sugar beet process, which is caused by higher conversion rates of the reacting components. It is also evident that the process always should include recirculation of monosaccharides, or a large amount of reactant would go to waste and the processes become much less efficient.

A reason for the yield of the process being lower than the theoretical yield is the equilibrium between glucose and fructose, which is present at 42% fructose when using glucose isomerase. Due to the equilibrium concentrations being higher in glucose than in fructose, this results in large amounts of glucose not isomerizing to fructose and thus not reacting to HMF. Recirculation of monosaccharides was implemented mainly to further utilize the glucose in the process. The chosen separation method to separate glucose, fructose, and other monosaccharides such as xylose and arabinose was chromatography, which can separate glucose and fructose to 90% purity of fructose. However, chromatography is not implemented in Aspen Plus which forced the use of a Sep-block to be implemented instead. The implementation of the Sep-block enabled the produced mass of HMF to increase from 80 kg/h to 194 kg/h in the wheat bran simulation, and from 33 kg/h to 58 kg/h in the sugar beet pulp simulation. As previously mentioned, the yields of HMF from the entirety of the dry raw materials rose from 8.0% to 19.4% for wheat bran and from 3.3% to 5.6% from sugar beet pulp by implementing recirculation of monosaccharides. If the recirculation would have been impossible to implement due to issues in the simulation, the unreacted glucose and fructose could have been used to produce other products, such as for example lactic acid or ethanol. Other possible products could derive from the remaining fractions of the raw material, such as protein obtained from the wheat bran. This would mean that more separation steps would need to be added. Therefore, the cost versus gain of producing several products must be investigated before implementation. However, it is clear that the recirculation of monosaccharides greatly benefitted the productivity and the economic viability of the processes.

When comparing the MISR diagrams, the overall conclusion is that the wheat bran process has higher values than the sugar beet pulp process for the comparable scenarios. At this stage of the process design, the wheat bran process has a greater financial viability than the sugar beet pulp process. At the used exchange rate of 1 USD = 8.3903 SEK, a selling price of \$24/kg HMF is needed to obtain MISR=1 when no monosaccharides are recirculated in the wheat bran simulation, while a selling price of \$33/kg HMF is needed when no monosaccharides are recirculated in the sugar beet pulp simulation.

Similarly, a selling price of \$10/kg HMF is needed to obtain MISR=1 when monosaccharides are recirculated in the wheat bran simulation, while a selling price of \$19/kg HMF is needed when monosaccharides are recirculated in the sugar beet pulp simulation. The average listed selling price of 1 kg HMF was \$240 when searched at Alibaba.com, which is substantially higher than the “break even” prices at MISR=1.

When investigating acceptable raw material prices, the wheat bran price must be below \$18.4/kg and \$45.6/kg before and after recirculation of monosaccharides, respectively, to have a MISR ratio >1. For sugar beet pulp, the raw material prices must be below \$7.63/kg and \$13.2/kg before and after recirculation to fulfill MISR >1. When comparing these prices to the ones used when varying the selling price of HMF, which was \$1.08/kg wheat bran and \$0.87/kg sugar beet pulp, it is highly unlikely that a high price of raw material would be the limiting factor in the profitability of the processes.

The difference between the two raw materials derives from the difference between the produced mass of HMF per hour, where the wheat bran process produces 2.45 and 3.44 times more HMF per hour than the sugar beet pulp process before and after implementation of recirculation respectively.

MISR is an indicator used to evaluate the profitability of a process quickly and simply and should only be used to find out whether to consider further evaluation or not. It is not an indicator to base an entire economic analysis upon. Considering the time constraints and the extension of economic analysis needed for this thesis, retrieving prices of chemicals from Alibaba.com is seen as acceptable. With that it should be said that another source for prices of the chemicals should be used in the future. To perform a more extensive economic analysis, another method must be used such as a more elaborate evaluation of operating costs, investment costs etc. This requires a larger collection of data than what is available from the process simulation performed in this thesis. Thus, a more detailed process simulation is needed to further evaluate the economic viability of the process.

Several of the reaction steps, such as steam explosion, enzymatic hydrolysis and acid hydrolysis would in reality be performed batch-wise, which could not be implemented in the process simulation due to time constraints. To assess the process more thoroughly, this is an example of an aspect to be added to a future, more elaborate, process simulation. Another aspect to investigate is that many components of the raw material were not available in Aspen Plus, which lead to the component properties being exchanged to those of similar components. It should thus be investigated if the exchange of properties results in fair results or not.

The process simulation has been made in a thorough way within the time frame. It also functions in a way that is very satisfactory with respect to the assumptions that had to be made. Going forward, a few things could be made to better the process simulation and make it more realistic. The first thing is to exchange blocks in the model to better alternatives. The chromatography unit that was implemented in the recirculation stream for monosaccharides is currently represented by a Sep-block but would greatly benefit from being exchanged to for example an Extract block. Other blocks that could be exchanged are the filter blocks that removes of the glucose isomerase after the isomerization reactor. In reality, other alternatives for the enzyme recovery may be required.

The distillation columns used in the final separation should also, as previously stated, be compared to other alternatives in the simulation stage of the process design, before building a pilot plant. The most crucial thing to improve the process simulation is the reactors, as no reaction kinetics at all were included in this thesis. As there is little to no kinetics available in literature, the key to going forward is to obtain more reaction kinetics to be able to implement this into Aspen Plus and exchanging RStoic with other suitable reactor blocks. Adding reaction kinetics to the Aspen Plus models would greatly benefit the reliability of the simulation, while also making it possible to perform more extensive economic analysis and, later, building a pilot plant.

## 6 Conclusions

Furans are used for a wide range of applications, such as chemical intermediates, chemical feedstocks for production of resins and polymers and as solvents. The main application for HMF is as a platform chemical, as it can be used as a renewable alternative for products currently produced from fossil resources. Examples of applications of chemicals that can be produced from HMF include monomers, resins, in textile dyes, in pharmaceuticals, and as flavors and fragrances.

Monosaccharides can be extracted from biomass by an array of different pretreatment methods. The ones investigated more closely in this thesis are steam explosion, acid hydrolysis and enzymatic hydrolysis, while other pretreatment methods include hydrotropic extraction, deep eutectic solvents, sodium hydroxide treatment, membrane filtration and extraction of starch with water. The two general steps for conversion of monosaccharides to HMF are isomerization of glucose to fructose and dehydration of fructose to HMF. HMF can be separated from the reaction mixture by extraction, crystallization, and adsorption. Distillation is also a possible separation process; however, it can be difficult due to the thermal instability of HMF at temperatures above 130°C and due to the low pressures required. Some of the by-products that can form during HMF production are humins, furfural, HMF dimers, levulinic acid, formic acid, acetic acid, 2-hydroxyacetyl furan, 1,2,4-trihydroxybenzene and fructose dianhydride. The by-products can be separated from HMF by adsorption or distillation. Other products similar to HMF that can also be produced from monosaccharides are succinic acid and levulinic acid.

Most of the thesis consisted of building two separate process simulation models for production of HMF from wheat bran and sugar beet pulp in Aspen Plus. The simulation showed that the different raw materials benefitted from different reactor steps, which in turn depends on the general composition of the raw material itself. The most apparent differences between the reactor steps needed for the two raw materials is in the pretreatment, where more monosaccharides were released by use of enzymatic hydrolysis for wheat bran and acid hydrolysis for sugar beet pulp. The rest of the reactor steps were the same used for the two raw materials: steam explosion, enzymatic isomerization using glucose isomerase and biphasic dehydration using hydrochloric acid and dimethyl carbonate. The conclusion of the process simulation is that the wheat bran process is the most effective in producing HMF in terms of yield, while also being consistently more economically viable at the investigated yearly production rate, even with varying inputs. The choice of reactor steps also resulted in less equipment demanded by the wheat bran process, which means that the investment cost would be lower than for the sugar beet pulp process. In the future, the process simulation could be improved by for example exchanging blocks into more realistic counterparts, as well as adding reaction kinetics.

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# Appendix

## Appendix A. Calculations made for the simple blocks process simulation

### A.1 Wheat bran

#### Steam explosion

Source states formation of 120.4 mg glucose/g dry wheat bran. 100 kg wheat bran in feed means that 12.04 kg glucose will be formed.

$$n(\text{Glucose formed})=68.89 \text{ mol}$$

$$n(\text{Cellulose, in})=221.41$$

1:1 molar relation cellulose:glucose means that  $n(\text{Cellulose, reacting})=68.89 \text{ mol}$

$$\text{Fractional conversion} = \frac{68.89 \text{ mol}}{221.41 \text{ mol}} = 0.302$$

#### Enzymatic hydrolysis

Bran:water ratio 1:5. In feed: 100 kg bran/h. 50 kg steam/h was added in the steam explosion, which means that 450 kg water/h need to be added.

1 l enzyme solution to 1 ton starch. Assume that starch equals the starch and cellulose fractions of the raw material for simplicity.

After steam explosion, 25.0546 kg cellulose/h is present. Add 0.025 l of enzymes.

38 g glucose/100 g dry matter. In feed:  $150 - 60.895 = 89.105 \text{ kg dry matter}$ .  $89.105 \cdot 0.38 = 33.8599 \text{ kg glucose}$ . There is only about 25 kg of cellulose present in the feed, the fractional conversion is set to 1.

#### Enzymatic isomerization

1 kg of enzymes gives 18 ton of 42% fructose.

In feed: 39.8888 kg glucose.  $\frac{39\,888.8 \text{ g}}{18\,000 \text{ g}} \approx 2.2 \text{ g enzyme needed for the conversion}$ .

## Biphasic dehydration

0.23 M HCl and 1:3 DMC:water (v/v). The fructose concentration is not adjusted to the one used in the literature.

Total volume flow:  $0.086003 \text{ m}^3/\text{h} = 86.003 \text{ dm}^3/\text{h}$ .

Use HCl with concentration  $12 \text{ mol}/\text{dm}^3$ .

$$c_1 V_1 = c_2 V_2 \Rightarrow 12 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 86.003 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 1.65 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{56.1111 \text{ kg}/\text{h}}{997 \text{ kg}/\text{m}^3} = 0.056 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.01876 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg}/\text{m}^3 \cdot 0.01876 \text{ m}^3/\text{h} = 20.1 \text{ kg DMC}/\text{h}$$

## **A.2 Sugar beet pulp**

### Steam explosion

The source states 10% solubilized glucose. Assume that only glucan reacts. Glucan has a mass fraction of 0.2043 in the raw material feed. The total flow of sugar beet pulp to the system is 100 kg, which means that 20.43 kg glucan is present in the raw material and 10 kg of glucose is formed. Thus, the fractional conversion of glucan is  $\frac{10 \text{ kg}}{20.43 \text{ kg}} = 0.49$

### Acid hydrolysis

50 kg of steam has been added in the steam explosion. The ratio of raw material:water should be 100:1500 (w:w). Add 1450 l of H<sub>2</sub>O/h.

Total flow of water and sugar beet pulp = 1600 l. 0.5% H<sub>2</sub>SO<sub>4</sub>·1600 l = add 8 l of H<sub>2</sub>SO<sub>4</sub>/h.

Total flow of water, sugar beet pulp and sulphuric acid = 1608 l. 10 kg of 1500 l in the feed is glucan.

$c_{\text{Glucan}} = \frac{10000 \text{ g}}{1500 \text{ l}} = 6.67 \text{ g}/\text{l}$ . 7.35 g glucose/l and 7.75 g fructose/l should be formed, the molar relation is 2:1:1 glucan:glucose:fructose. There is not enough glucan to react to the extent that it should, the fractional conversion is set to form equal amounts of glucose and fructose.

### Chemical isomerization

The source states 10% glucose in water (w/w) for the use of Sn- $\beta$ .

$$\dot{m}_{Tot} = 1605.91 \text{ kg/h}, \dot{m}_{H_2O} = 1501.42 \text{ kg/h}, \dot{m}_{Glucose} = 16.9114 \text{ kg/h}.$$

$$\frac{16.9114 \text{ kg}}{0.1} \approx 169 \text{ kg/h}. \dot{m}_{Glucose \text{ and fructose}} = 22.69983 \text{ kg/h}. \text{ Remove } 1355 \text{ kg H}_2\text{O/h}.$$

Catalyst: glucose:Sn- $\beta$  1:50 molar ratio. Molar flow of glucose: 93.8703 mol/h, add 1.88 mol of Sn- $\beta$ /h.

### Biphasic dehydration

The source states 30 % (w/v) fructose, 0.23 M HCl and 1:3 DMC:water (v/v).

Assume that the water weighs 1 kg/l. The total flow should be 36.8 kg/h.

$\dot{m}_{Glucose \text{ and fructose}} = 22.69983 \text{ kg/h}$ .  $36.8 - 22.69983 = 14.07 \text{ kg/h}$  of H<sub>2</sub>O in the stream, the excess water is removed.

Total volume flow: 31.0124 dm<sup>3</sup>/h.

Use HCl with concentration 12 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 12 \frac{\text{mol}}{\text{dm}^3} \cdot V_{HCl} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 31.0124 \text{ dm}^3 \Rightarrow V_{HCl} = 0.59 \text{ dm}^3$$

$$\dot{V}_{H_2O} = \frac{\dot{m}_{H_2O}}{\rho_{H_2O}} = \frac{14.0247 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.014 \text{ m}^3/\text{h}.$$

$$\dot{V}_{DMC} = \frac{1}{3} \cdot \dot{V}_{H_2O} = 0.004689 \text{ m}^3/\text{h}.$$

$$\dot{m}_{DMC} = \rho_{DMC} \cdot \dot{V}_{DMC} = 1070 \text{ kg/m}^3 \cdot 0.004689 \text{ m}^3/\text{h} = 5.02 \text{ kg DMC/h}$$

## Appendix B. Additional process simulation inputs in the advanced blocks simulation

### B.1 Wheat bran

#### B.1.1 Reactors

Table B.1.1-a. Specifications for the heater blocks connected to the biphasic dehydration reaction blocks.

Aspen Plus Block	Heater <i>BIPCOOL1</i>	Heater <i>BIPCOOL3</i>
Temperature	50°C	50°C
Pressure	1 bar	1 bar

Table B.1.1-b. Specifications for the separation blocks connected to the biphasic dehydration reaction blocks.

Aspen Plus Block	<i>BIPH2OS1</i>	<i>BIPH2OS2</i>	<i>BIPH2OS3</i>	<i>BIPH2OS4</i>
Name of specified outlet stream	<i>BH2OSEP1</i>	<i>BH2OSEP2</i>	<i>BH2OSEP3</i>	<i>BH2OSEP4</i>
Specifications	Volume flow of water: 1.51 m <sup>3</sup> /h	Volume flow of water: 0.28 m <sup>3</sup> /h	Volume flow of water: 2.81 m <sup>3</sup> /h	Volume flow of water: 0.52 m <sup>3</sup> /h

Table B.1.1-c. Specifications for the separation blocks connected to the heterogeneous catalyst dehydration reaction blocks.

Aspen Plus Block	<i>AMBH2OS1-4, FEH2OS1-4</i>
Name of specified outlet stream	<i>AMH2OS1-4, FEH2OS1-4</i>
Specifications	Split fraction of water: 1

### B.1.2 Separation and recirculation

Table B.1.2-a. Component mass flows in the stream exiting the pretreatment reactors in the wheat bran advanced blocks simulation.

<b>Component</b>	<b>Component mass flow (kg/h)</b>
Water	5091.91
Protein	158
Fat	37
Cellulose	78.925
Arabinoxylan	230.815
$\beta$ -glucan	17.875
Phenolic acid	11
Ash	58
Enzyme	0.178
Glucose	316.265
Arabinose	0.0524998
Xylose	0.157499

Table B.1.2-b. Component mass flows in the stream exiting the isomerization reactor in the wheat bran advanced blocks simulation.

<b>Component</b>	<b>Component mass flow (kg/h)</b>
Water	5036.19
Enzyme	0.0176
Glucose	181.427
Fructose	131.377
Arabinose	0.0519253
Xylose	0.155776

*Table B.1.2-c. Summarization of the design specification used on the FLASH1 block in the wheat bran advanced blocks simulation.*

**Define** Stream variable, mass flow of water in stream *TO-DEHYD*

**Spec** Target: 220 kg/h, tolerance: 5 kg/h

**Vary** Temperature in block *FLASH1* between 25-125°C

*Table B.1.2-d. Component mass flows in the stream exiting the dehydration reactor in the wheat bran advanced blocks simulation.*

<b>Component</b>	<b>Component mass flow (kg/h)</b>
Water	269.559
Glucose	181.427
Fructose	4.59818
HCl	3.71899
Formic acid	2.91501
Levulinic acid	7.35417
DMC	78.3
HMF	80.7596
Arabinose	0.0518346
Xylose	0.155774

*B.1.3 Heat recovery system, utilities, and pressure changers*

*Table B.1.3-a. Specifications of cooling water streams entering HEX2, HEX3, HEX4 and HEX6 in the wheat bran simulation.*

<b>Name of stream</b>	<b>CH2O2IN</b>	<b>CH2O3IN</b>	<b>CH2O4IN</b>	<b>CH2O6IN</b>
<b>To block</b>	<i>HEX2</i>	<i>HEX3</i>	<i>HEX4</i>	<i>HEX6</i>
<b>Temperature</b>	20°C	20°C	20°C	20°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	2000 kg/h	31000 kg/h	2000 kg/h	1200 kg/h
<b>Mass fraction</b>	H <sub>2</sub> O: 1			

*Table B.1.3-b. Specifications of HP-steam used in HEX8, HEX9 and HEX10 in the wheat bran simulation.*

<b>Used in block</b>	<b>HEX8</b>	<b>HEX9</b>	<b>HEX10</b>
<b>Temperature and vapor fraction at inlet</b>	250°C	250°C	250°C
<b>Temperature and vapor fraction at outlet</b>	249°C, 0	249°C, 0	249°C, 0
<b>Mass flow used for heating of cold stream</b>	320.242 kg/h	52.2491 kg/h	0.65694 kg/h

## B.2 Sugar beet pulp

### B.2.1 Reactors

*Table B.2.1-a. Specifications for the heater blocks in the pretreatment section of the flowsheet.*

<b>Aspen Plus Block</b>	<b>Heater <i>AH-COOL1</i></b>	<b>Heater <i>EH-COOL1</i></b>
<b>Temperature</b>	25°C	25°C
<b>Pressure</b>	1 bar	1 bar

*Table B.2.1-b. Specifications for the separation blocks in the isomerization section of the flowsheet.*

<b>Aspen Plus Block</b>	<b>Sep <i>CISH2OS1</i></b>	<b>Sep <i>CISH2OS2</i></b>
<b>Name of specified outlet stream</b>	<i>CH2OS1</i>	<i>CH2OS2</i>
<b>Specifications</b>	Mass flow rate of water: 5189 kg/h  Split fraction of glucose and fructose: 0	Mass flow rate of water:  8043 kg/h

*Table B.2.1-c. Specifications for the heater blocks connected to the biphasic dehydration reaction blocks.*

<b>Aspen Plus Block</b>	<b>Heater <i>BIPCOOL1</i></b>	<b>Heater <i>BIPCOOL3</i></b>
<b>Temperature</b>	50°C	50°C
<b>Pressure</b>	1 bar	1 bar

Table B.2.1-d. Specifications for the separation blocks connected to the biphasic dehydration reaction blocks.

<b>Aspen Plus Block</b>	<b><i>BIPH2OS1</i></b>	<b><i>BIPH2OS2</i></b>	<b><i>BIPH2OS3</i></b>	<b><i>BIPH2OS4</i></b>
<b>Name of specified outlet stream</b>	<i>BH2OSEP1</i>	<i>BH2OSEP2</i>	<i>BH2OSEP3</i>	<i>BH2OSEP4</i>
<b>Specifications</b>	Volume flow of water: 0.46 m <sup>3</sup> /h, split fraction of glucose, fructose, mannose: 0	Volume flow of water: 5.76 m <sup>3</sup> /h	Volume flow of water: 1.06 m <sup>3</sup> /h	Split fraction of water: 0.991  Split fraction of glucose and fructose: 0

Table B.2.1-e. Specifications for the separation blocks connected to the heterogeneous catalyst dehydration reaction blocks.

<b>Aspen Plus Block</b>	<b>AMBH2OS1-4, FEH2OS1-4</b>
<b>Name of specified outlet stream</b>	AMH2OS1-4, FE-H2OS1-4
<b>Specifications</b>	Split fraction of water: 1

## B.2.2 Separation and recirculation

Table B.2.2-a. Component mass flows in the stream exiting the pretreatment reactors in the sugar beet pulp advanced blocks simulation.

<b>Component</b>	<b>Component mass flow (kg/h)</b>
Glucan	145.222
Xylan	43.1323
Galactan	44.1254
Arabinan	213.57
Mannan	16.65
Pectin	6.1668
Lignin	10.44
Protein	102.78
Ash	22.59
Water	4313.11
Glucose	56.1915
Fructose	35.3138
Arabinose	218.343
Xylose	3.5543
Galactose	10.0701
H <sub>2</sub> SO <sub>4</sub>	41.4538

Table B.2.2-b. Component mass flows in the stream exiting the isomerization section of the sugar beet pulp advanced blocks simulation.

Component	Component mass flow (kg/h)
Water	2525.9
Enzyme	0.003
Glucose	32.1698
Fructose	58.1525
Arabinose	96.2384
Xylose	3.50836
Galactose	9.93997
H <sub>2</sub> SO <sub>4</sub>	0.00824792

Table B.2.2-c. Summarization of the design specification used on the FLASH2 block in the sugar beet pulp advanced blocks simulation.

<b>Define</b>	Stream variable, mass flow of water in stream <i>TO-DEHYD</i>
<b>Spec</b>	Target: 50 kg/h, tolerance: 1 kg/h
<b>Vary</b>	Temperature in block <i>FLASH2</i> between 25-150°C

*Table B.2.2-d. Component mass flows in the stream exiting the dehydration reactor in the sugar beet pulp advanced blocks simulation.*

<b>Component</b>	<b>Component mass flow (kg/h)</b>
Water	70.9337
Glucose	32.1697
Fructose	2.03534
Arabinose	95.7218
Xylose	3.50822
Galactose	9.93994
HCl	1.44954
H <sub>2</sub> SO <sub>4</sub>	0.00818959
Formic acid	1.2903
Levulinic acid	3.25525
DMC	17.8
HMF	35.7474

*B.2.3 Heat recovery system, utilities, and pressure changers*

*Table B.2.3-a. Specifications of LP-steam used in HEX2, HEX3, HEX4 and HEX5 for the sugar beet pulp simulation.*

<b>Used in block</b>	<b><i>HEX2</i></b>	<b><i>HEX3</i></b>	<b><i>HEX4</i></b>	<b><i>HEX5</i></b>
<b>Temperature and vapor fraction at inlet</b>	125°C, 1	125°C, 1	125°C, 1	125°C, 1
<b>Temperature and vapor fraction at outlet</b>	124°C, 0	124°C, 0	124°C, 0	124°C, 0
<b>Mass flow used for heating of cold stream</b>	2055.55 kg/h	59.3575 kg/h	1.68121 kg/h	13.9004 kg/h

*Table B.2.3-b. Specifications of cooling water streams entering HEX6, HEX7, HEX8 and HEX10 in the sugar beet pulp simulation.*

<b>Name of stream</b>	<b><i>CH206IN</i></b>	<b><i>CH207IN</i></b>	<b><i>CH208IN</i></b>	<b><i>CH2010IN</i></b>
<b>To block</b>	<i>HEX6</i>	<i>HEX7</i>	<i>HEX8</i>	<i>HEX10</i>
<b>Temperature</b>	20°C	20°C	20°C	20°C
<b>Pressure</b>	1 bar	1 bar	1 bar	1 bar
<b>Total flow rate</b>	10000 kg/h	5135 kg/h	5000 kg/h	400 kg/h
<b>Mass fraction</b>	H <sub>2</sub> O: 1			

*Table B.2.3-c. Specifications of HP-steam used in HEX11, HEX12 and HEX13 in the sugar beet pulp simulation.*

<b>Used in block</b>	<b><i>HEX11</i></b>	<b><i>HEX12</i></b>	<b><i>HEX13</i></b>
<b>Temperature and vapor fraction at inlet</b>	250°C, 1	250°C, 1	250°C, 1
<b>Temperature and vapor fraction at outlet</b>	249°C, 0	249°C, 0	249°C, 0
<b>Mass flow used for heating of cold stream</b>	15.5794 kg/h	100.592 kg/h	0.123744 kg/h

## Appendix C. Calculations made for the advanced blocks reactor simulation – wheat bran

### Steam explosion

Time and temperature: 200°C, 120 s. Design specification resulted in steam flow = 285 kg/h, 200°C, vapor fraction = 1.

$$120.4 \text{ mg glucose/g dry wheat bran} = \frac{0.1204 \text{ g}}{1 \text{ g}} \Rightarrow \text{Conversion} = 12.04\%$$

$$1000 \text{ kg wheat bran/h} \Rightarrow 120.4 \text{ kg glucose/h}$$

In the wheat bran, only starch (mass fraction = 0.249), cellulose (mass fraction = 0.11) and  $\beta$ -glucan (mass fraction = 0.025) can react to glucose.

Of 1000 kg wheat bran/h, starch, cellulose and  $\beta$ -glucan is 384 kg/h.

Of the 384 kilos that can react,

$$\text{starch is} = \frac{249 \text{ kg}}{384 \text{ kg}} = 0.648, \text{ cellulose is} = \frac{110 \text{ kg}}{384 \text{ kg}} = 0.2864 \text{ and } \beta\text{-glucan is} = \frac{25 \text{ kg}}{384 \text{ kg}} = 0.065.$$

Molar relations: starch:glucose 1:1.1, cellulose:glucose 1:1,  $\beta$ -glucan:glucose 1:1.1

$0.648 \cdot 120.4 = 78.07$  kg of the glucose comes from the starch. 78.07 kg glucose = 433.7 mol glucose. 1:1.1 relation means that 394.3 mol starch is consumed.  $n(\text{starch in feed}) = 1382.12$  mol, fractional conversion =  $\frac{394.3 \text{ mol}}{1382.12 \text{ mol}} = 0.285$

$0.2864 \cdot 120.4 = 34.49$  kg of the glucose comes from the cellulose. 34.49 kg glucose = 191.6 mol glucose. 1:1 relation means that 191.6 mol cellulose is consumed.  $n(\text{cellulose in feed}) = 678.416$  mol, fractional conversion =  $\frac{191.6 \text{ mol}}{678.416 \text{ mol}} = 0.282$

$0.065 \cdot 120.4 = 7.83$  kg of the glucose comes from the  $\beta$ -glucan. 7.84 kg glucose = 43.28 mol glucose. 1:1.1 relation means that 39.5 mol  $\beta$ -glucan is consumed.  $n(\beta\text{-glucan, feed}) = 138.767$  mol, fractional conversion =  $\frac{39.5 \text{ mol}}{138.767 \text{ mol}}$

Xylose and arabinose are formed from arabinoxylan which has a mass fraction of 0.231 in the feed. 60 mg xylose/100 g dry matter and 20 mg arabinose/100 g dry matter is formed.

Molar relations: arabinoxylan:xylose 1:1.12, arabinoxylan:arabinose 1:1.12

$$n(\text{Arabinoxylan in feed}) = 1538.65 \text{ mol/h}$$

$$\text{Mass of xylose formed: } 231 \text{ kg} \cdot \frac{0.06 \text{ kg}}{100 \text{ kg}} = 0.1386 \text{ kg. } M(\text{Xylose}) = 150 \text{ g/mol} \Rightarrow n(\text{Xylose}) = 0.924 \text{ mol} \Rightarrow n(\text{Arabinoxylan}) = 0.825 \text{ mol. Fractional conversion} = \frac{0.825 \text{ mol}}{1538.65 \text{ mol}} = 5.36 \cdot 10^{-4}$$

Mass of arabinose formed:  $231 \text{ kg} \cdot \frac{0.02 \text{ kg}}{100 \text{ kg}} = 0.0462 \text{ kg}$ .  $M(\text{Arabinose}) = 150 \text{ g/mol} \Rightarrow n(\text{Arabinose}) = 0.308 \text{ mol} \Rightarrow n(\text{Arabinoxylan}) = 0.275 \text{ mol}$ . Fractional conversion =  $\frac{0.275 \text{ mol}}{1538.65 \text{ mol}} = 1.82 \cdot 10^{-4}$

### Acid hydrolysis

2% H<sub>2</sub>SO<sub>4</sub> per weight of slurry. Assuming slurry = what is present after steam explosion = 1285 kg/h. 2% H<sub>2</sub>SO<sub>4</sub> of 1285 kg = 25.7 kg 100% H<sub>2</sub>SO<sub>4</sub>/h or 51.4 kg 50% H<sub>2</sub>SO<sub>4</sub>/h.

7.5 g glucose per 100g starch free residue, which is assumed to be the entire flow minus glucose and starch. Mass of starch free residue = 701.353 kg/h.

Total mass of glucose formed =  $0.075 \cdot 701.353 \text{ kg/h} = 52.6 \text{ kg/h}$

Cellulose after steam explosion = 78.925 kg/h,  $\beta$ -glucan after steam explosion = 17.875 kg/h. In total, 96.8 kg that can react to glucose.

Of the 96.8 kg that reacts, cellulose is  $\frac{78.925 \text{ kg}}{96.8 \text{ kg}} = 0.815$  and  $\beta$ -glucan is  $\frac{17.875 \text{ kg}}{96.8 \text{ kg}} = 0.185$ .

Molar relations: cellulose:glucose 1:1,  $\beta$ -glucan:glucose = 1:1.1

$0.815 \cdot 52.6 \text{ kg} = 42.89 \text{ kg}$  of the glucose comes from the cellulose.  $42.89 \text{ kg glucose} = 238.3 \text{ mol glucose} \Rightarrow 238.3 \text{ mol cellulose reacts}$ .  $n(\text{Cellulose in feed}) = 486.763 \text{ mol} \Rightarrow$  Fractional conversion =  $\frac{238.3 \text{ mol}}{486.763 \text{ mol}} = 0.489$

$0.185 \cdot 52.6 \text{ kg} = 9.71 \text{ kg}$  of the glucose comes from the  $\beta$ -glucan.  $9.71 \text{ kg glucose} = 53.96 \text{ mol glucose} \Rightarrow 49.05 \text{ mol } \beta\text{-glucan reacts}$ .  $n(\beta\text{-glucan in feed}) = 99.2186 \text{ mol} \Rightarrow$  Fractional conversion =  $\frac{49.05 \text{ mol}}{99.2186 \text{ mol}} = 0.4944$

Arabinoxylan is assumed to react to xylose and arabinose. 10 g of xylose is formed per 100g starch free residue, 8 g of arabinose is formed per 100g starch free residue. Of the starch free residue, 230.834 kg is arabinoxylan.

Molar relations: arabinoxylan:xylose 1:1.12, arabinoxylan:arabinose 1:1.12

$n(\text{Arabinoxylan in feed}) = 1537.55 \text{ mol/h}$

Total mass of xylose formed =  $701.353 \text{ kg} \cdot 0.1 = 70.1353 \text{ kg/h}$ .  $M(\text{Xylose}) = 150 \text{ g/mol} \Rightarrow n(\text{Xylose formed}) = 467.57 \text{ mol} \Rightarrow$  Fractional conversion of arabinoxylan = 0.2715

Total mass of arabinose formed =  $701.353 \text{ kg} \cdot 0.08 = 56.10824 \text{ kg/h}$ .  $M(\text{Arabinose}) = 150 \text{ g/mol} \Rightarrow n(\text{Arabinose formed}) = 374.055 \text{ mol} \Rightarrow$  Fractional conversion of arabinoxylan = 0.22

### Enzymatic hydrolysis

1 l enzyme per ton of starch yields 38 g glucose/100 g dry matter. Mass of starch in feed is 178.035 kg. 1 l per 1000 kg means that 0.178 l enzyme is needed per 178.035 kg starch. Assume that the enzyme solution has the density of water.

Only the starch reacts to glucose. Dry matter is assumed to be everything in the wheat bran except the water = 769.669 kg.  $0.38 \cdot 769.669 \text{ kg} = 292.47422 \text{ kg}$  glucose is formed =  $n(\text{Glucose}) = 1624.856 \text{ mol}$ .

Molar relation: starch:glucose 1:1.1

$\Rightarrow n(\text{Starch that reacts}) = 1477 \text{ mol}$ .  $n(\text{Starch, available}) = 988.218 \text{ mol} \Rightarrow$  Fractional conversion = 1.

Bran:water ratio 1:5. 285 kg of steam has been added in steam explosion, all of which is assumed to have condensed. 4715 kg of water is added to the enzymatic hydrolysis.

### Chemical isomerization

10 % (w/w) glucose in water. 1:50 molar ratio Sn- $\beta$ :glucose.

*CATISO1 – after steam explosion and acid hydrolysis*

Water balance: 173.118 kg glucose/h. 10% concentration gives a total mass flow of 1731.18 kg/h. Add 1156.438 kg of water.

Molar flow of glucose: 960.925 mol/h.  $1:50 = \frac{960.925 \text{ mol}}{50} =$  add 19.2185 mol of Sn- $\beta$ .

*CATISO2 – after steam explosion and enzymatic hydrolysis*

Water balance: 316.795 kg glucose/h. 10% concentration gives a total mass flow of 3167.95 kg/h. Add 2108.44 kg of water.

Molar flow of glucose: 1755.49 mol/h.  $1:50 = \frac{1755.49 \text{ mol}}{50} =$  add 35.1098 mol of Sn- $\beta$ .

### Enzymatic isomerization

*EISO1 – after steam explosion and acid hydrolysis*

Glucose: 173.118 kg/h = 173 118 g/h.

1 g of enzyme gives 18 000 g of 42% fructose.

$$\frac{173\,118\,g}{18\,000\,g} = 9.62 \text{ g of enzyme will result in 173.118 kg 42\% fructose and 58\% glucose.}$$

*EISO2 – after steam explosion and enzymatic hydrolysis*

Glucose: 316.795 kg/h = 316 795 g/h.

1 g enzyme gives 18 000 g of 42% fructose.

$$\frac{316\,795\,g}{18\,000\,g} = 17.6 \text{ g of enzyme will result in 316.795 kg 42\% fructose and 58\% glucose.}$$

### Biphasic dehydration

30% fructose in water (w/v). 1:3 DMC:water volume ratio. 0.23 M HCl.

*BIPH1 – after steam explosion, acid hydrolysis, chemical isomerization*

Total flow of 1.73096 m<sup>3</sup>/h after cooling. 53.6662 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{53\,666.2 \text{ g}}{1\,730\,960 \text{ ml solution}} = 3.1\% \Rightarrow 30\% = \frac{53\,666.2 \text{ g}}{178\,887 \text{ ml solution}}$$

178 887 ml  $\approx$  0.179m<sup>3</sup>. Remove 1.55 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 179 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 6.86 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{50.9666 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.051 \text{ m}^3/\text{h.}$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.017 \text{ m}^3/\text{h.}$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.017 \text{ m}^3/\text{h} = 18.2 \text{ kg DMC/h}$$

*BIPH2 – after steam explosion, acid hydrolysis, enzymatic isomerization*

Total flow of 0.536397 m<sup>3</sup>/h. 72.7089 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{72\,708.9 \text{ g}}{536\,397 \text{ ml solution}} = 13.6\% \Rightarrow 30\% = \frac{72\,708.9 \text{ g}}{242\,363 \text{ ml solution}}$$

242 363 ml  $\approx$  0.242 m<sup>3</sup>. Remove 0.294 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 242 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 9.28 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{110.143 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.110 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.036 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.036 \text{ m}^3/\text{h} = 39.4 \text{ kg DMC/h}$$

*BIPH3 – after steam explosion, enzymatic hydrolysis, chemical isomerization*

Total flow of 3.16226 m<sup>3</sup>/h after cooling. 98.0411 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{98\,041.1 \text{ g}}{3\,162\,260 \text{ ml solution}} = 3.1\% \Rightarrow 30\% = \frac{98\,041.1 \text{ g}}{326\,803.67 \text{ ml solution}}$$

326 803.67 ml  $\approx$  0.3268 m<sup>3</sup>. Remove 2.84 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 326.8 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 12.5 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{47.0915 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.047 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.0157 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.0157 \text{ m}^3/\text{h} = 16.8 \text{ kg DMC/h}$$

*BIPH4 – after steam explosion, enzymatic hydrolysis, enzymatic isomerization*

Total flow of 0.9843 m<sup>3</sup>/h. 132.83 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{132\,830 \text{ g}}{984\,300 \text{ ml solution}} = 13.5\% \Rightarrow 30\% = \frac{132\,830 \text{ g}}{442\,766.67 \text{ ml solution}}$$

442 766.67 ml  $\approx$  0.44 m<sup>3</sup>. Remove 0.54 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 440 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 17 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{218.955 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.22 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.073 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.073 \text{ m}^3/\text{h} = 78.3 \text{ kg DMC/h}$$

### Heterogenic catalyst dehydration

3 wt.% fructose in DMSO. 6 wt.% catalyst relative to substrate. The calculations for the amberlyst 15 powder catalyst reactor and the FePW<sub>12</sub>O<sub>40</sub> catalyst reactor are the same since the feed to the reactors with the same combination of reactors upstream are the same.

*AMB1 and FE1 – after steam explosion, acid hydrolysis, chemical isomerization*

After separation of water – 53.6662 kg fructose. 3% fructose  $\Rightarrow$  total flow of 1789 kg/h. The total flow to the reactor is 173.118 kg/h, which means that 1616 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 53.6662 kg fructose  $\cdot$  6% = 3.22 kg catalyst/h

*AMB2 and FE2 – after steam explosion, acid hydrolysis, enzymatic isomerization*

After separation of water – 72.7089 kg fructose. 3% fructose  $\Rightarrow$  total flow of 2423.63 kg/h. The total flow to the reactor is 173.117 kg/h, which means that 2250.513 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 72.7089 kg fructose  $\cdot$  6% = 4.36 kg catalyst/h

*AMB3 and FE3 – after steam explosion, enzymatic hydrolysis, chemical isomerization*

After separation of water – 98.0411 kg fructose. 3% fructose  $\Rightarrow$  total flow of 3268.04 kg/h. The total flow to the reactor is 316.264 kg/h, which means that 2952 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 98.0411 kg fructose  $\cdot$  6% = 5.88 kg catalyst/h

*AMB4 and FE4 – after steam explosion, enzymatic hydrolysis, enzymatic isomerization*

After separation of water – 132.83 kg fructose. 3% fructose  $\Rightarrow$  total flow of 4427.67 kg/h. The total flow to the reactor is 316.264 kg/h, which means that 4111.4 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 132.83 kg fructose  $\cdot$  6% = 7.97 kg catalyst/h

## Appendix D. Calculations made for the advanced blocks reactor simulation – sugar beet pulp

### Steam explosion

Design specification resulted in steam flow = 285 kg/h, 210°C, vapor fraction = 1.

10% solubilized glucose. Assuming conversion of glucan → glucose = 10%

97% solubilized arabinose. Assuming conversion of pectin → arabinose = 97%

### Acid hydrolysis

15% solid loading (w/v), 0.5% H<sub>2</sub>SO<sub>4</sub> (v/v).

In feed: 1000 kg of solid material, added 285 kg steam in steam explosion that has condensed.

$$\frac{\text{Weight (g)}}{\text{Volume (100 ml)}} = 0.15 \Rightarrow \frac{1\,000\,000\text{ g}}{6\,670\,000\text{ ml}} = 0.15$$

6 670 000 ml = 6.67 m<sup>3</sup>, volume in = 1.23 m<sup>3</sup> assumed to be only water. Add 5.44 m<sup>3</sup> H<sub>2</sub>O/h.

0.5% H<sub>2</sub>SO<sub>4</sub> (v/v): 6.67 m<sup>3</sup> · 0.5% = 33.4 l H<sub>2</sub>SO<sub>4</sub>/h.

From the acid hydrolysis, 7.35 g glucose/l, 7.75 g fructose/l, 0.78 g xylose/l and 2.21 g galactose/l are formed.

Total number of litres in the system = 6713.4 l

m(Fructose formed)=52 028.85 g, n(Fructose formed)=289.049167 mol

m(Glucose formed)=49 343.49 g, n(Glucose formed)=274.1305

n(Glucan in feed)=1134 mol, n(Sucrose in feed)=71.7791 mol

At total conversion of sucrose, 71.7791 mol of glucose and 71.7791 mol fructose is formed, which is not the entirety of the fraction that is formed in the literature. The remaining part is assumed to be formed from glucan.

Fractional conversion of sucrose to glucose and fructose = 1

$$\text{Fractional conversion of glucan to glucose} = \frac{202.3514\text{ mol}}{1134\text{ mol}} = 0.178$$

$$\text{Fractional conversion of glucan to fructose} = \frac{217.270067\text{ mol}}{1134\text{ mol}} = 0.1916$$

Xylose is assumed to be formed from xylan, molar relation xylan:xylose 1:1, galactose is assumed to be formed from galactan, molar relation galactan:galactose 1:1.1

m(Xylose formed)=5236.452 g, n(Xylose formed)=34.90968 mol

$$n(\text{Xylan in feed})=350.147 \text{ mol. Fractional conversion of xylan} = \frac{34.90968 \text{ mol}}{350.147 \text{ mol}} = 0.0997$$

$$m(\text{Galactose formed})=14\ 836.614 \text{ g, } n(\text{Galactose formed})=82.4256333 \text{ mol}$$

$$n(\text{Galactan in feed})=295.744 \text{ mol. Fractional conversion of galactan} = \frac{74.9323939 \text{ mol}}{295.744 \text{ mol}} = 0.2534$$

### Enzymatic hydrolysis

10% (w/v) initial solids, 0.1 ml enzyme/g glucan → 9.62 g/l glucose.

In feed: 1000 kg of solid material, added 285 kg steam in steam explosion that has condensed.

$$\frac{\text{Weight (g)}}{\text{Volume (100 ml)}} = 0.1 \Rightarrow \frac{1\ 000\ 000 \text{ g}}{10\ 000\ 000 \text{ ml}} = 0.1$$

10 000 000 ml = 10 m<sup>3</sup>, volume in = 1.23 m<sup>3</sup> assumed to be only water. Add 8.77 m<sup>3</sup> of H<sub>2</sub>O/h.

183.87 kg glucan = 183 870 g glucan. 0.1 ml/g · 183 870 g = 18 387 ml = 18.4 l enzyme.

$$V_{\text{tot}} = 10 \text{ m}^3 + 18.4 \text{ l} = 10\ 018.387 \text{ l} \approx 10.02 \text{ m}^3$$

$$9.62 \text{ g/l} \cdot 10\ 018.387 \text{ l} = 96\ 376.88294 \text{ g glucose} = 96.38 \text{ kg} \Rightarrow n(\text{Glucose})=535.427 \text{ mol.}$$

$$n(\text{Glucan in feed})=1134 \text{ mol. Fractional conversion of glucan} = \frac{535.427 \text{ mol}}{1134 \text{ mol}} = 0.47$$

### Chemical isomerization

10 % (w/w) glucose in water. 1:50 molar ratio Sn-β:glucose.

*CATISO1 – after steam explosion and acid hydrolysis*

Water balance: 72.0786 kg glucose/h. 10% concentration gives a total mass flow of 720.786 kg/h. Total mass flow before water removal = 5907.08 kg/h. Remove 5186 kg of water.

$$\text{Molar flow of glucose: } 400.086 \text{ mol/h. } 1:50 = \frac{400.086 \text{ mol}}{50} = \text{add } 8 \text{ mol of Sn-}\beta.$$

*CATISO2 – after steam explosion and enzymatic hydrolysis*

Water balance: 118.721 kg glucose/h. 10% concentration gives a total mass flow of 1187.21 kg/h. Total mass flow before water removal = 9226.48 kg/h. Remove 8039 kg of water.

$$\text{Molar flow of glucose: } 658.984 \text{ mol/h. } 1:50 = \frac{658.984 \text{ mol}}{50} = \text{add } 13.18 \text{ mol of Sn-}\beta.$$

### Enzymatic isomerization

*EISO1 – after steam explosion and acid hydrolysis*

Glucose: 72.0786 kg/h = 72 078.6 g/h.

1 g of enzyme gives 18 000 g of 42% fructose.

$$\frac{72\,078.6\text{ g}}{18\,000\text{ g}} = 4\text{ g of enzyme will result in 72.0786 kg 42\% fructose and 58\% glucose.}$$

*EISO2 – after steam explosion and enzymatic hydrolysis*

Glucose: 118.721 kg/h = 118 721 g/h.

1 g enzyme gives 18 000 g of 42% fructose.

$$\frac{118\,721\text{ g}}{18\,000\text{ g}} = 6.6\text{ g of enzyme will result in 118.721 kg 42\% fructose and 58\% glucose.}$$

### Biphasic dehydration

30% fructose in water (w/v). 1:3 DMC:water volume ratio. 0.23 M HCl.

*BIPH1 – after steam explosion, acid hydrolysis, chemical isomerization*

Total flow of 0.711516 m<sup>3</sup>/h after cooling. 74.419 kg fructose in feed.

$$\% \text{ w/v} = \frac{\text{g solute}}{100 \text{ ml solution}} = \frac{74\,419\text{ g}}{711\,516\text{ ml solution}} = 10.5\% \Rightarrow 30\% = \frac{74\,419\text{ g}}{248\,063\text{ ml solution}}$$

248 063 ml  $\approx$  0.248 m<sup>3</sup>. Remove 0.46 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 248 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 9.5 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{149.214 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.15 \text{ m}^3/\text{h.}$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.05 \text{ m}^3/\text{h.}$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.05 \text{ m}^3/\text{h} = 53.4 \text{ kg DMC/h}$$

*BIPH2 – after steam explosion, acid hydrolysis, enzymatic isomerization*

Total flow of 6.03553 m<sup>3</sup>/h. 82.3476 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{82\,347.6 \text{ g}}{6\,035\,530 \text{ ml solution}} = 1.4\% \Rightarrow 30\% = \frac{82\,347.6 \text{ g}}{274\,492 \text{ ml solution}}$$

274 492 ml  $\approx$  0.274 m<sup>3</sup>. Remove 5.76 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 274 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 10.5 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{177.247 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.178 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.059 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.059 \text{ m}^3/\text{h} = 63.4 \text{ kg DMC/h}$$

*BIPH3 – after steam explosion, enzymatic hydrolysis, chemical isomerization*

Total flow of 1.18682 m<sup>3</sup>/h after cooling. 36.8032 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{36\,803.2 \text{ g}}{1\,186\,820 \text{ ml solution}} = 3.1\% \Rightarrow 30\% = \frac{36\,803.2 \text{ g}}{122\,677 \text{ ml solution}}$$

122 677 ml  $\approx$  0.123 m<sup>3</sup>. Remove 1.06 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 123 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 4.7 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{40.4606 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.041 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.0135 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.0135 \text{ m}^3/\text{h} = 14.5 \text{ kg DMC/h}$$

*BIPH4 – after steam explosion, enzymatic hydrolysis, enzymatic isomerization*

Total flow of 9.37801 m<sup>3</sup>/h. 49.549 kg fructose in feed.

$$\% \text{ w/v} = \frac{g \text{ solute}}{100 \text{ ml solution}} = \frac{49\,549 \text{ g}}{9\,378\,010 \text{ ml solution}} = 0.5\% \Rightarrow 30\% = \frac{49\,549 \text{ g}}{165\,163 \text{ ml solution}}$$

165 163 ml  $\approx$  0.165 m<sup>3</sup>. Remove 9.21 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 165 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 6.3 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{81.4795 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.082 \text{ m}^3/\text{h}.$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.027 \text{ m}^3/\text{h}.$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.027 \text{ m}^3/\text{h} = 29.1 \text{ kg DMC/h}$$

### Heterogenic catalyst dehydration

3 wt.% fructose in DMSO. 6 wt.% catalyst relative to substrate. The calculations for the amberlyst 15 powder catalyst reactor and the FePW<sub>12</sub>O<sub>40</sub> catalyst reactor are the same since the feed to the reactors with the same combination of reactors upstream are the same.

*AMB1 and FE1 – after steam explosion, acid hydrolysis, chemical isomerization*

After separation of water – 74.419 kg fructose. 3% fructose  $\Rightarrow$  total flow of 2480 kg/h. The total flow to the reactor is 124.153 kg/h, which means that 2356 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 74.419 kg fructose  $\cdot$  6% = 4.47 kg catalyst/h

*AMB2 and FE2 – after steam explosion, acid hydrolysis, enzymatic isomerization*

After separation of water – 82.3476 kg fructose. 3% fructose  $\Rightarrow$  total flow of 2744.92 kg/h. The total flow to the reactor is 124.153 kg/h, which means that 2621 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 82.3476 kg fructose  $\cdot$  6% = 4.94 kg catalyst/h

*AMB3 and FE3 – after steam explosion, enzymatic hydrolysis, chemical isomerization*

After separation of water – 36.8032 kg fructose. 3% fructose  $\Rightarrow$  total flow of 1227 kg/h. The total flow to the reactor is 118.721 kg/h, which means that 1108 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 36.8032 kg fructose  $\cdot$  6% = 2.21 kg catalyst/h

*AMB4 and FE4 – after steam explosion, enzymatic hydrolysis, enzymatic isomerization*

After separation of water – 49.549 kg fructose. 3% fructose  $\Rightarrow$  total flow of 1651.63 kg/h. The total flow to the reactor is 117.974 kg/h, which means that 1534 kg DMSO/h needs to be added.

Catalyst: 6 wt.% relative to substrate. 49.549 kg fructose  $\cdot$  6% = 2.97 kg catalyst/h

## Appendix E. Comparison of the reactor combinations simulated with advanced blocks

The streams are named after the combination of reactor steps the streams have undergone. Here follows an explanation of the used abbreviations: SE = steam explosion, AH = acid hydrolysis, EH = enzymatic hydrolysis, CI = isomerization using chemical catalyst, EI = isomerization using enzyme, BI = biphasic dehydration, AMB = heterogeneous dehydration using Amberlyst 15 powder catalyst, FE = heterogeneous dehydration using FePW<sub>12</sub>O<sub>40</sub> catalyst. The most effective combinations in terms of yield of HMF from the raw material and the reacting fraction of the raw material respectively are marked with green. The reactor combination chosen for further simulations is marked with green in the “combination” row.

WHEAT BRAN															
Combination	SE+AH+CI+BI	SE+AH+CI+AMB	SE+AH+CI+FE	SE+AH+EI+BI	SE+AH+EI+AMB	SE+AH+EI+FE	SE+EH+CI+BI	SE+EH+CI+AMB	SE+EH+CI+FE	SE+EH+EI+BI	SE+EH+EI+AMB	SE+EH+EI+FE			
Mass of HMF	32,9895	37,5671	36,4401	44,6954	50,8973	49,3704	60,2679	68,6305	66,5716	81,6534	92,9834	90,1939	Mass of raw material	1000	kg/h
Yield, raw material to HMF (%)	3,299	3,757	3,644	4,47	5,09	4,937	6,027	6,863	6,657	8,165	9,298	9,019	Mass of reacting fraction, wheat bran	384	kg
Yield of reacting fraction of raw material to HMF (%)	8,591	9,783	9,49	11,639	13,255	12,857	15,695	17,873	17,336	21,264	24,214	23,488	(Starch + cellulose + beta-glucan)		
	SE+AH+CI			SE+AH+EI			SE+EH+CI			SE+EH+EI					
Mass of fructose	53,6661			72,7089			98,0415			132,83					
Yield of raw material to fructose (%)	5,367			7,271			9,804			13,283					
Yield of reacting fraction of raw material to fructose (%)	13,976			18,935			25,532			34,591					
SUGAR BEET PULP															
Combination	SE+AH+CI+BI	SE+AH+CI+AMB	SE+AH+CI+FE	SE+AH+EI+BI	SE+AH+EI+AMB	SE+AH+EI+FE	SE+EH+CI+BI	SE+EH+CI+AMB	SE+EH+CI+FE	SE+EH+EI+BI	SE+EH+EI+AMB	SE+EH+EI+FE	Mass of reacting fraction, sugar beet pulp (Glucan + sucrose)	228,87	kg
Mass of HMF	45,7467	52,0944	50,5316	50,6205	57,6445	55,9152	22,6235	25,7627	24,9898	30,4587	34,685	33,6445			
Yield, raw material to HMF (%)	4,575	5,209	5,053	5,062	5,764	5,592	2,262	2,576	2,499	3,046	3,469	3,364			
Yield of reacting fraction of raw material to HMF (%)	19,988	22,762	22,079	22,118	25,187	24,431	9,885	11,256	10,919	13,308	15,155	14,7			
	SE+AH+CI			SE+AH+EI			SE+EH+CI			SE+EH+EI					
Mass of fructose	74,419			82,3476			36,8031			49,8622					
Yield of raw material to fructose (%)	7,442			8,235			3,68			4,986					
Yield of reacting fraction of raw material to fructose (%)	32,516			35,98			16,08			21,786					

## Appendix F. Calculations made for the advanced blocks separation and recycling system simulation – wheat bran

### Recalculation of fractional conversions in the steam explosion reactor

Arabinoxylan was changed from xylose to xylan, and because of their different molecular weights the fractional conversion must be recalculated.



$n(\text{Arabinoxylan, feed})=1538.65 \text{ mol/h}$ ,  $m(\text{Arabinoxylan, feed})=231 \text{ kg/h}$

Xylose: 60 mg/100g dry matter.  $2.31 \cdot 0.06 \text{ kg}=0.1386 \text{ kg}$  xylose is formed, which equals 0.924 mol xylose. The conversion of arabinoxylan is  $\frac{0.924 \text{ mol}}{1538.65 \text{ mol}} = 0.0006$ .

Arabinose: 20 mg/100g dry matter.  $2.31 \cdot 0.02 \text{ kg}=0.0462 \text{ kg}$  arabinose is formed, which equals 0.308 mol xylose. The conversion of arabinoxylan is  $\frac{0.308 \text{ mol}}{1538.65 \text{ mol}} = 0.0002$ .

### Recalculation of amount of enzyme in enzymatic isomerization

Glucose:  $312.805 \text{ kg/h} = 312\,805 \text{ g/h}$

1 g enzyme gives 18000 g product.

$\frac{312\,805 \text{ g}}{18\,000 \text{ g}} = 17.4 \text{ g}$  enzyme for conversion. In the reactor simulation the result was 17.6 g, and the difference is considered small enough to disregard.

## Appendix G. Calculations made for the advanced blocks separation and recycling system simulation – sugar beet pulp

### Recalculation acid hydrolysis

15% solid loading (w/v), 0.5% H<sub>2</sub>SO<sub>4</sub> (v/v).

In feed: 680.177 kg of solid material, added 285 kg steam in steam explosion that has condensed.

$$\frac{\text{Weight (g)}}{\text{Volume (100 ml)}} = 0.15 \Rightarrow \frac{680\,177\text{ g}}{4\,534\,513.333\text{ ml}} = 0.15$$

4 534 513.333 ml = 4.53 m<sup>3</sup>, volume in feed of liquid = 0.567 m<sup>3</sup> assumed to be only water. Add 3.96 m<sup>3</sup> H<sub>2</sub>O/h.

0.5% H<sub>2</sub>SO<sub>4</sub> (v/v): 4.53 m<sup>3</sup> · 0.5% = 22.67 l H<sub>2</sub>SO<sub>4</sub>/h.

From the acid hydrolysis, 7.35 g glucose/l, 7.75 g fructose/l, 0.78 g xylose/l and 2.21 g galactose/l are formed.

Total number of litres in the system = 4552.67 l

m(Fructose formed)=35 283.1925 g, n(Fructose formed)=196.017736 mol

m(Glucose formed)=33 462.1245 g, n(Glucose formed)=185.900692

n(Glucan in feed)=1134 mol, n(Sucrose in feed)=71.7791 mol

At total conversion of sucrose, 71.7791 mol of glucose and 71.7791 mol fructose is formed, which is not the entirety of the fraction that is formed in the literature. The remaining part is assumed to be formed from glucan.

Fractional conversion of sucrose to glucose and fructose = 1

Fractional conversion of glucan to glucose =  $\frac{114.121592\text{ mol}}{1134\text{ mol}} = 0.1006$

Fractional conversion of glucan to fructose =  $\frac{124.238636\text{ mol}}{1134\text{ mol}} = 0.1096$

Xylose is assumed to be formed from xylan, molar relation xylan:xylose 1:1, galactose is assumed to be formed from galactan, molar relation galactan:galactose 1:1.1

m(Xylose formed)=3551.0826 g, n(Xylose formed)=23.673884 mol

n(Xylan in feed)=350.147 mol. Fractional conversion of xylan =  $\frac{23.673884\text{ mol}}{350.147\text{ mol}} = 0.0676$

m(Galactose formed)=10 061.4007 g, n(Galactose formed)=55.8966706 mol

$$n(\text{Galactan in feed})=295.744 \text{ mol. Fractional conversion of galactan} = \frac{55.8966706 \text{ mol}}{295.744 \text{ mol}} = 0.1718$$

### Recalculation of amount of enzyme in enzymatic isomerization

Glucose: 55.4666 kg/h = 55 466.6 g/h

1 g enzyme gives 18000 g product.

$$\frac{55\,466.6 \text{ g}}{18\,000 \text{ g}} \approx 3 \text{ g enzyme for conversion.}$$

### Recalculations for the dehydration reactor

Total flow of 2.76168 m<sup>3</sup>/h. 58.1525 kg fructose in feed.

$$\% \text{ w/v} = \frac{\text{g solute}}{100 \text{ ml solution}} = \frac{58\,152.5 \text{ g}}{2\,761\,680 \text{ ml solution}} = 2\% \Rightarrow 30\% = \frac{58\,152.5 \text{ g}}{193\,841 \text{ ml solution}}$$

193 841 ml  $\approx$  0.194 m<sup>3</sup>. Remove 2.57 m<sup>3</sup> H<sub>2</sub>O.

Use HCl with concentration 6 mol/dm<sup>3</sup>.

$$c_1 V_1 = c_2 V_2 \Rightarrow 6 \frac{\text{mol}}{\text{dm}^3} \cdot V_{\text{HCl}} = 0.23 \frac{\text{mol}}{\text{dm}^3} \cdot 194 \text{ dm}^3 \Rightarrow V_{\text{HCl}} = 7.44 \text{ dm}^3$$

$$\dot{V}_{\text{H}_2\text{O}} = \frac{\dot{m}_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} = \frac{50 \text{ kg/h}}{997 \text{ kg/m}^3} = 0.05 \text{ m}^3/\text{h.}$$

$$\dot{V}_{\text{DMC}} = \frac{1}{3} \cdot \dot{V}_{\text{H}_2\text{O}} = 0.0166 \text{ m}^3/\text{h.}$$

$$\dot{m}_{\text{DMC}} = \rho_{\text{DMC}} \cdot \dot{V}_{\text{DMC}} = 1070 \text{ kg/m}^3 \cdot 0.0166 \text{ m}^3/\text{h} = 17.8 \text{ kg DMC/h}$$

## Appendix H. Calculations of the theoretical yield of HMF from wheat bran and sugar beet pulp

### Wheat bran

Reactions present in the formation of HMF:

1. Starch + H<sub>2</sub>O → 1.11 glucose
2. Cellulose + H<sub>2</sub>O → glucose
3. β-glucan + H<sub>2</sub>O → 1.11 glucose
4. Glucose → fructose
5. Fructose → HMF + 3 H<sub>2</sub>O

Total mass flow into system is 1000 kg/h. Of this, the fractions of starch, cellulose and β-glucan is 0.249, 0.11 and 0.025 respectively. In total, 384 kg/h of the raw material is the reacting fraction. The molar flow of each component is 1382.12, 678.416 and 138.767 mol/h.

$$M(\text{Starch}), M(\beta\text{-glucan}) = 180.158018 \text{ g/mol}$$

$$M(\text{Cellulose}) = 162.142402 \text{ g/mol}$$

$$M(\text{Glucose}), M(\text{Fructose}) = 180.156 \text{ g/mol}$$

$$M(\text{HMF}) = 126.11 \text{ g/mol}$$

$$M(\text{H}_2\text{O}) = 18.02 \text{ g/mol}$$

Reaction 1 forms 1534.1532 mol glucose/h, reaction 2 forms 678.416 mol glucose/h and reaction 3 forms 152.6437 mol glucose/h. In total, 2365.2129 mol glucose/h can be formed.

Reaction 4 forms 2365.2129 mol fructose/h.

Reaction 5 forms 2365.2129 mol HMF/h, which equals 298.28 kg HMF/h.

Thus, the yield of HMF from the raw material is  $\frac{298.276999 \text{ kg/h}}{1000 \text{ kg/h}} \approx 29.8\%$ , and the yield of HMF from the reacting fraction of the raw material is  $\frac{298.276999 \text{ kg/h}}{384 \text{ kg/h}} \approx 77.7\%$ .

## Sugar beet pulp

Reactions present in the formation of HMF:

1. Cellulose + H<sub>2</sub>O → glucose
2. Sucrose + H<sub>2</sub>O → glucose fructose
3. Glucose → fructose
4. Fructose → HMF + 3 H<sub>2</sub>O

Total mass flow into system is 1000 kg/h. Of this, the fractions of glucan and sucrose is 0.2043 and 0.02457 respectively. In total, 228.87 kg/h of the raw material is the reacting fraction. The molar flow of each component is 1260 and 71.7791 mol/h.

$$M(\text{Cellulose}) = 162.142402 \text{ g/mol}$$

$$M(\text{Sucrose}) = 342.300196 \text{ g/mol}$$

$$M(\text{Glucose}), M(\text{Fructose}) = 180.156 \text{ g/mol}$$

$$M(\text{HMF}) = 126.11 \text{ g/mol}$$

$$M(\text{H}_2\text{O}) = 18.02 \text{ g/mol}$$

Reaction 1 forms 1260 mol glucose/h, reaction 2 forms 71.7791 mol glucose/h and 71.7791 mol fructose/h. In total, 1331.7791 mol glucose can be formed per hour.

Reaction 3 forms 1331.7791 mol fructose/h. In total, 1403.5582 mol fructose/h can be formed.

Reaction 4 forms 1403.5582 mol HMF/h, which equals 177.00 kg HMF/h.

Thus, the yield of HMF from the raw material is  $\frac{177.00 \text{ kg/h}}{1000 \text{ kg/h}} \approx 17.7\%$ , and the yield of HMF from the reacting fraction of the raw material is  $\frac{177.00 \text{ kg/h}}{228.87 \text{ kg/h}} \approx 77.3\%$ .

## Appendix I. Calculations of the yield of HMF from wheat bran and sugar beet pulp obtained in the process simulations

### Wheat bran, before monosaccharide recirculation

Total mass of wheat bran fed per hour = 1000 kg. Of this, starch is 0.249, cellulose is 0.11 and  $\beta$ -glucan is 0.025. The total feed of the reacting fraction of wheat bran is 384 kg/h.

In the product stream, the mass of produced HMF is 79.9798 kg/h.

$$\text{Yield of HMF from raw material} = \frac{79.9798 \text{ kg/h}}{1000 \text{ kg/h}} = 0.0799 \approx 8.0\%$$

$$\text{Yield of HMF from the reacting fraction of the raw material} = \frac{79.9798 \text{ kg/h}}{384 \text{ kg/h}} = 0.208 \approx 21\%$$

### Wheat bran, after monosaccharide recirculation

Total mass of wheat bran fed per hour = 1000 kg. Of this, starch is 0.249, cellulose is 0.11 and  $\beta$ -glucan is 0.025. The total feed of the reacting fraction of wheat bran is 384 kg/h.

In the product stream, the mass of produced HMF is 193.842 kg/h.

$$\text{Yield of HMF from raw material} = \frac{193.842 \text{ kg/h}}{1000 \text{ kg/h}} = 0.1938 \approx 19.4\%$$

$$\text{Yield of HMF from the reacting fraction of the raw material} = \frac{193.842 \text{ kg/h}}{384 \text{ kg/h}} = 0.505 = 50.5\%$$

### Sugar beet pulp, before monosaccharide recirculation

Total mass of sugar beet pulp fed per hour = 1000 kg. Of this, glucan is 0.2043 and sucrose is 0.02457. The total feed of the reacting fraction of sugar beet pulp is 228.87 kg/h.

In the product stream, the mass of produced HMF is 32.6108 kg/h.

$$\text{Yield of HMF from raw material} = \frac{32.6108 \text{ kg/h}}{1000 \text{ kg/h}} = 0.0326 \approx 3.3\%$$

$$\text{Yield of HMF from the reacting fraction of the raw material} = \frac{32.6108 \text{ kg/h}}{228.87 \text{ kg/h}} = 0.142 \approx 14\%$$

### Sugar beet pulp, after monosaccharide recirculation

Total mass of sugar beet pulp fed per hour = 1000 kg. Of this, glucan is 0.2043 and sucrose is 0.02457. The total feed of the reacting fraction of sugar beet pulp is 228.87 kg/h.

In the product stream, the mass of produced HMF is 56.2781 kg/h.

$$\text{Yield of HMF from raw material} = \frac{56.2781 \text{ kg/h}}{1000 \text{ kg/h}} = 0.0563 \approx 5.6\%$$

$$\text{Yield of HMF from the reacting fraction of the raw material} = \frac{56.2781 \text{ kg/h}}{228.87 \text{ kg/h}} = 0.246 \approx 24.6\%$$