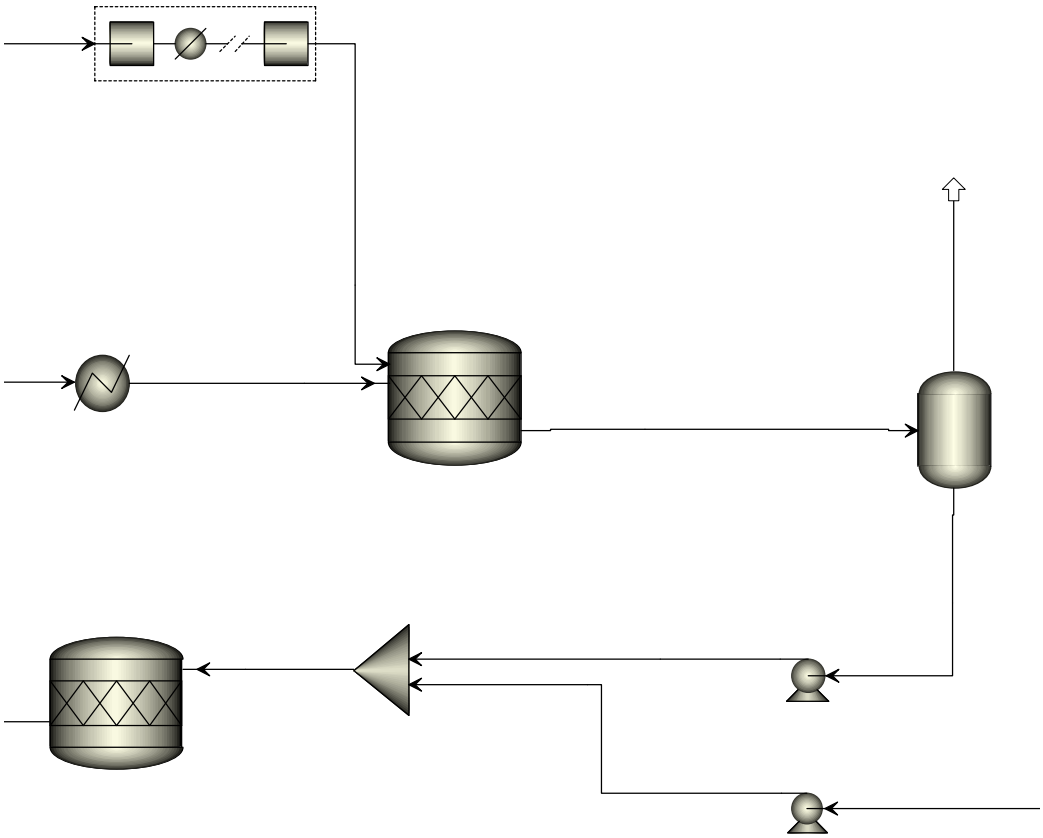
Upscaling of FDCA Synthesis from HMF to an Industrial Scale



Linnéa Wahlberg

Department of Chemical Engineering

Master Thesis 2020

LUND UNIVERSITY

Upscaling of FDCA Synthesis from HMF to an Industrial Scale

by

Linnéa Wahlberg

Department of Chemical Engineering
Lund University

June 2020

Supervisor: **Professor Christian Hulteberg**
Co-supervisor: **Professor Rajni Hatti-Kaul**
Examiner: **Professor Ola Wallberg**

Postal address
P.O. Box 124
SE-221 00 Lund, Sweden
Web address
www.chemeng.lth.se

Visiting address
Getingevägen 60

Telephone
+46 46-222 82 85
+46 46-222 00 00
Telefax
+46 46-222 45 26

Preface

This project was made possible thanks to the support of the Department of Chemical Engineering at the Faculty of Engineering, Lund University. I am grateful for the advice given, and interest shown, by my peers and supervisors.

Abstract

To support the transition into green plastics, the upscaling and economic analysis of 2,5-furandicarboxylic acid (FDCA) synthesis from 5-hydroxymethylfurfural (HMF) was done. The project can be described as a plant-to-plastics process, with sugar beet-derived HMF as a starting point. The final product in this upscaled process can be further processed into polyethylene 2,5-furandicarboxylate (PEF). PEF is a polymer with better properties than PET, better gas barrier properties to mention some, which could lead to reduced plastics consumption since less material is needed for the same end-use. The oxidation of FDCA is catalysed by the enzymes PaoABC, GOase$M_{3\text{-}5}$, HRP and catalse, with a 100 % yield. Operating conditions are mild; 37 °C and 4.9 bar(a) and the process design is kept fairly simple due to the lack of by-products which reduces the need for downstream process equipment. There is a total annual cost for the FDCA production of 4867 MSEK, which gives a cost of 24,300 SEK/tonne. The components affecting the overall cost of production the most is the feedstock and reagents. Out of the reagents it is the enzymes used for catalysis that are responsible for the majority of the cost.

Sammanfattning

För att underlätta övergången till bioplast har en uppskalning, följt av en ekonomisk utvärdering, gjorts av produktionen av 2,5-furandikarboxylsyra (FDCA) från 5-hydroxymetylfurfural (HMF). HMF framställs från sockerbetan och projektet kan beskrivas som en från-gröda-till-plast-process. FDCA som är slutprodukten i denna uppskalade process, kan vidare omvandlas till polyetylen 2,5-furandikarboxylat (PEF). PEF är en polymer med bättre egenskaper än PET, bättre barriär-egenskaper för att nämna någon, vilket kan leda till en minskad plastförbrukning eftersom mindre material behövs för samma användningsområde. Oxidationen av HMF till FDCA är katalyserad av enzymerna PaoABC, GOase$M_{3\text{-}5}$, HRP och katalas, med ett utbyte på 100 %. Reaktionen sker vid de milda betingelserna 37 °C och 4.9 bar(a) and processdesignen hålls relativt simpel tack vare att inga biprodukter bildas vilket minskar behövet av utrustning för upprening. Totala årskostnaden för produktionen av FDCA är 4867 MSEK, vilket motsvarar en kostnad på 24,300 SEK/ton. Det som har störst inverkan på den totala kostnaden är inköpen av råmaterial samt övriga reagens. Bland de övriga reagensen så står enzymerna som katalyserar reaktionen för majoriteten av kostnaden.

Table of Contents

Table of Abbreviations

DFF	2,5-Diformylfuran
FDCA	2,5-Furandicarboxylic acid
FFCA	5-Formylfuran-2-carboxylic acid
GOase M_{3-5}	Galactose oxidase M_{3-5}
HMF	5-Hydroxymethylfurfural
HMFCA	5-Hydroxymethyl-2-furan carboxylic acid
HRP	Horseradish peroxidase
PaoABC	Periplasmic aldehyde oxidase ABC
PBT	Polybutylene terephthalate
PEF	Polyethylene 2,5-furandicarboxylate
PET	Polyethylene terephthalate
PTA	Polyterephthalic acid

1 Introduction

1.1 Introduction

The request for sustainable usage of the planet's resources to reduce global warming is growing. Fossil fuels, and the products derived thereof, must be replaced by greener alternatives for the sake of the climate. This is where bio-based plastics play an important role.

The widely used chemical 2,5-furandicarboxylic acid (FDCA) can be derived from biomaterials, and progress is needed in the field to increase conversion of the feedstock while maintaining a high yield. One of the most promising areas of use is the pursuit of green substitutes to the polyethylene terephthalate (PET) polymers to reduce the consumption of fossil-based materials. FDCA can be converted into polymers suitable for applications where PET is used today.

1.2 Purpose

Currently, the bottleneck to the green alternative, PEF, is the achieving an efficient production on an industrial scale. Therefore, one of the steps from sugar to polyethylene 2,5-furandicarboxylate (PEF) will be examined in this report. The starting point will be 5-hydroxymethylfurfural (HMF), produced from sugar, and the end product will be FDCA. The focus will be of doing an industrial-scale process design that can produce a sufficient amount of FDCA. A sufficient amount is here defined as a quantity large enough to be used for substitution of a current PET market share.

1.3 Aim

The aim of the project is to scale up the already existing FDCA synthesis with HMF as a starting point, through simulations, to an industrial scale. With PEF considered a greener alternative to PET, it is believed to be wise to incorporate a sustainable way of thinking wherever possible. The sugar production in northern Europe is used to estimate feedstock supply and the European PET market is observed. These factors are used as a foundation when deciding the production volume. To narrow it all down, the following research questions will be addressed:

1. What is a suitable production volume and plant size?
2. What is a suitable process design and what is the capital cost for the chosen equipment?
3. What is the operating cost of FDCA production?

1.4 Scope

The scope of the project is to scale-up the FDCA synthesis from HMF, through simulations in ASPEN Plus. From this simulation, a detailed design will be suggested, and a cost analysis will be done thereof. The suggested design will also include sizing and specification of the equipment types needed. Excluded from the scope is the in-depth investigation of HMF production, the production of enzymes and other parameters affecting the enzymatic catalysis and the conversion of FDCA to PEF.

1.5 Disposition

In the report, the reader will first be introduced to relevant background information including, but not limited to, an overview of the preceding HMF synthesis and the increased strain on the current sugar production, the conversion of HMF to FDCA and information about the catalysing enzymes used for the production. Lastly, the properties of PEF are explained and compared to those of PET. In the sections regarding materials and methods, the ASPEN Plus simulation will be shown together with the assumptions upon which the report is built. The results section presents the equipment (including size, specifications and bare module cost), the amounts and costs of the reagents used as well as the economic analysis. Finally, a discussion of the results is given, a conclusion to answer the research questions and suggestions on future work that needs to be done.

2 Background

To give the reader an understanding of the process, a background to the project is presented below.

2.1 HMF Synthesis

HMF is a precursor to FDCA, which can be produced from entirely biological carbon sources, to reduce the use of fossil-based material (Chen, *et al.*, 2016). The molecular structure of HMF can be seen in Figure 2.1.

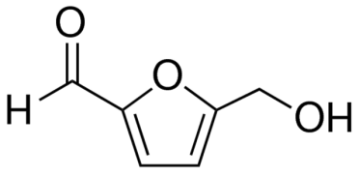


Figure 2.1. Molecular structure of 5-hydroxymethylfurfural (HMF).

The reaction is often acid-catalysed and to ensure that the acid does not degrade the HMF, the pH should not be too low. The choice of acid in HMF synthesis from sugar was found to not influence the maximum yield of HMF that much, but rather affect the reaction rate (Körner, *et al.*, 2018). The following data was found in the literature review and is presented in Table 2.1.

Table 2.1. Conversion and yield, found in literature, for HMF synthesis from sugar.

Feedstock	$Yield_{HMF}$ (%)	Solvent	Catalyst	Reference
Glucose	63.3	Water-butanol	Glucose isomerase & HCl	(Fang, *et al.*, 2017, p. 98)
Fructose	78	Subcritical acetone-water mix	H_2SO_4	(Fang, *et al.*, 2017, p. 87)
Sucrose	88.2	[BMIM]Cl	[bi-C_3SO_3HMIM][CH_3SO_3] & $MnCl_2$	(Fang, *et al.*, 2017, p. 105)

Other catalysts that are possible to use for HMF synthesis are solid acids, or acids of organic nature and mineral acids, as well as metallic catalysts. Other media that the reaction can be carried out in are ionic liquids, two-phase systems, organic solvents and aqueous media. (Fang, *et al.*, 2017, p. 81)

2.1.1 Using Sugar – A Renewable Feedstock

Sugars, as well as other types of bio-based materials, have been found suitable for HMF synthesis. The sugars can be derived from various feedstocks, such as lignocellulosic biomass or from the sugar beet, and both mono- and polysaccharides have been used (Chheda, *et al.*, 2007).

2.1.2 The Sugar Market

The sugar (sucrose) production in the northern parts of Europe is dominated by Nordzucker. From 2013 to 2018, there has been an average annual sugar production of 2.5 million tonnes (Nordzucker AG, 2017/2018).

To be able to estimate the amount of available feedstock, it is assumed that between 1-5 % of Nordzucker's annual sugar production can be applied for this purpose. This equals a feedstock supply of 25,000-125,000 tonnes per year.

2.2 About FDCA

FDCA is a heterocyclic molecule with two carboxylic acid side chains placed in the *para*-positions, Figure 2.2. The compound is generally found in the urine and in blood plasma of humans. FDCA has been used in various productions, such as of fungicides and succinic acid. It is also seen as a good chemical building block for polyamides, polyesters and plasticizers. Other polyesters that can be produced from FDCA, except from PEF, are polybutylene terephthalate (PBT) and PET. (Sajid, *et al*., 2018)

The United States Department of Energy added FDCA to their top twelve significant bio-based chemicals (Werpy & Petersen, 2004), thanks to the potential and versatility of this platform chemical.

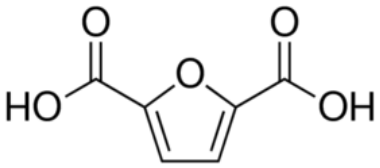


Figure 2.2. Molecular structure of 2,5-Furandicarboxylic acid (FDCA).

2.3 FDCA Synthesis from HMF

Today, there are several different ways to produce FDCA from HMF. The commonly used routes are catalysed by various compounds. Some use oxygen from air and others use noble metals or metal salts. (Dijkman, *et al*., 2014) Many catalysts tend to be expensive and rare and requires inconvenient temperatures or pressures as well as possible additives. A more sustainable way could be the bio-catalytic route. Using bio-catalysts is favourable due to the fairly cheap and highly selective reactions under mild conditions (Yuan, *et al*., 2020).

The general reaction of HMF being converted to FDCA, where oxygen is used and water is the by-product, can be described as shown in Equation 1/Figure 2.3 (Eerhart, *et al*., 2012).

$$HMF + \frac{3}{2}O_2 \rightarrow FDCA + H_2O \quad (1)$$

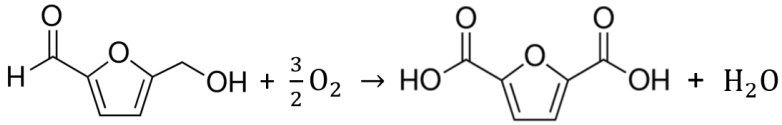


Figure 2.3. Simplified reaction where HMF and oxygen forms FDCA and water.

If making a closer observation, there are several intermediates when HMF is oxidized into FDCA. These are 2,5-diformylfuran (DFF). 5-hydroxymethyl-2-furan carboxylic acid (HMFCA) and 5-formylfuran-2-carboxylic acid (FFCA), which can be seen in Figure 2.4.

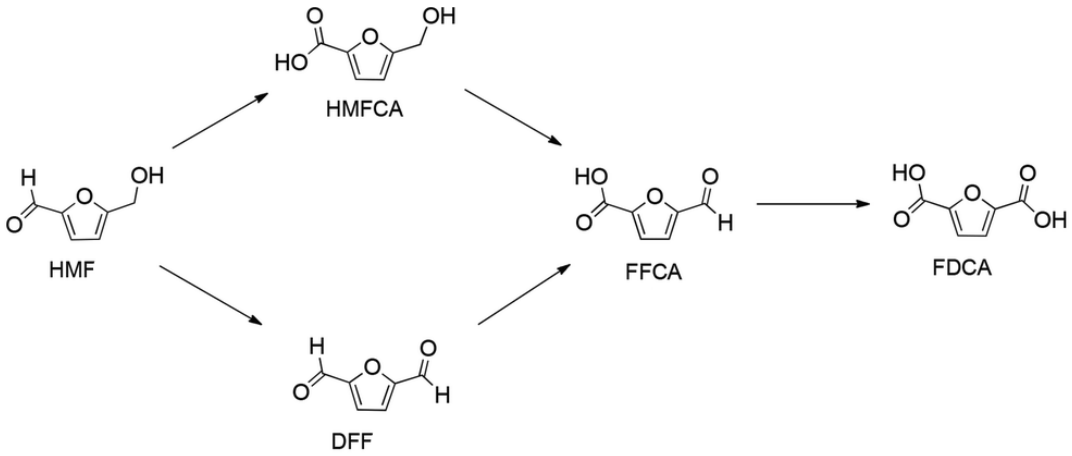


Figure 2.4. Oxidation of HMF to FDCA with intermediates.

2.3.1 Enzyme-Catalysed FDCA Synthesis

To fully oxidize HMF to FDCA, the enzyme need to work on both the aldehyde and the alcohol groups (Zhang & Deng, 2015). If this is done better by one enzyme alone or several enzymes working together and resulting in an efficient reaction both regarding time and yield, can be discussed.

In literature it was found that a combination of the four enzymes periplasmic aldehyde oxidase ABC (PaoABC), Galactose oxidase $M_{3\text{-}5}$ (GOase $M_{3\text{-}5}$), horseradish peroxidase (HRP) and catalase resulted in a 100 % yield in a continuous one-pot reaction arrangement in 6 hours. PaoABC and GOase $M_{3\text{-}5}$ in combination with HRP oxidize HMF to HMFCA and DFF respectively. HMFCA is further oxidized by GOase $M_{3\text{-}5}$ in combination with HRP to FFCA. To produce the final product FDCA, PaoABC is catalysing both reactions from DFF via FFCA to FDCA. The HRP is used due to its ability to activate GOase and results in a better yield and activity. Catalase is added to the reaction mixture to degrade the hydrogen peroxide formed, to maintain good reaction conditions. Removing the hydrogen peroxides allows the reaction rate to increase, thus a higher HMF concentration can be used. (McKenna, *et al.*, 2017) The reaction is described in Figure 2.5.

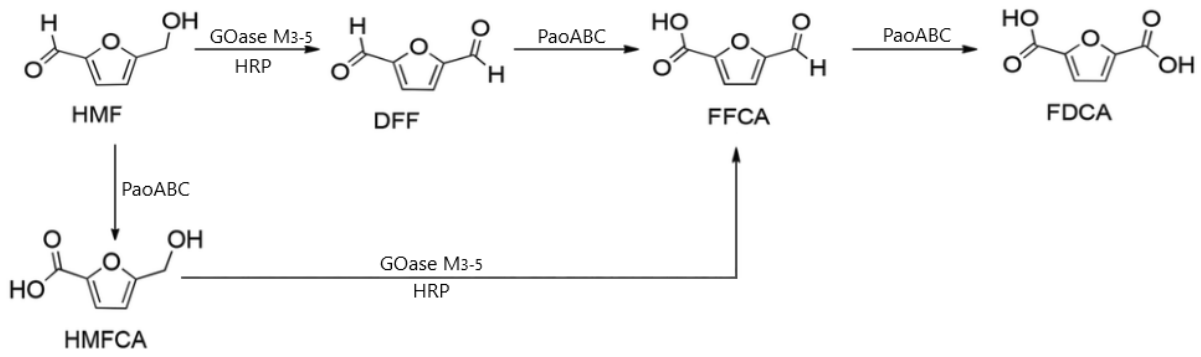


Figure 2.5. The enzyme catalyzed oxidation of HMF to FDCA with oxygen from air. GOase M_{3-5}, HRP and PaoABC are added in, together with catalase that degrades the H_2O_2 formed during the process.

The reaction was carried out in 0.2 M potassium phosphate buffer, at 37 °C and pH 7.0 that was regulated with NaOH. The specific enzyme concentrations are listed in Table 2.2 and the HMF concentration was 100 mM. However, the enzymes showed the same catalytic effect at 200 mM when being immobilized, see the following section. (McKenna, *et al.*, 2017)

Table 2.2. The enzymes and in which concentration they were used in the reactions yielding 100 % FDCA in 6 hours (McKenna, et al., 2017).

Enzyme	Concentration (mg/mL)
PaoABC	28.9
GOase M3-5	3.0
Catalase	3.3
HRP	1.0

Immobilization of Enzymes

Combined-cross linked enzyme aggregates (combi-CLEAs) are constructions that allow two or more enzymes to be immobilized (McKenna, *et al.*, 2017). These have shown to be very promising for continuous productions that are enzyme catalysed. Furthermore, it could lead to great cost reductions due to simpler reuse, recycling and separation of the enzymes (Cao, *et al.*, 2003). Attempts by McKenna *et al.* (2017) failed to form successful combi-CLEAs with PaoABC and catalase, but further trials were done. The most effective combination was a CLEA of catalase and gel captured PaoABC that showed no reduction in yield during while being recycled 14 times. This combination was successful with substrate levels as high as 200 mM.

With immobilized enzymes it could be possible to use other types of continuous reactors.

2.4 FDCA – A Precursor to PEF

It is found that FDCA can be further processed to form PEF, to mention one of the potential products. PEF is formed when FDCA is catalytically polymerized together with ethylene glycol. (Sajid, *et al*., 2018) Ethylene glycol and FDCA reacts to form PEF and water (Eerhart, *et al.*, 2012), described in the unbalanced Equation 2 below.

$$FDCA + EG \rightarrow PEF + H_2O \quad (2)$$

The large-scale production of PEF from FDCA is an on-going project. Avantium is currently building a plant that is supposed to be able to deliver 5000 tonnes annually by 2023, located in Holland (Avantium, 2020). In this plant, the reaction is believed to be supported by a heterogeneous catalyst. (Sajid, *et al.*, 2018) To make the large-scale production economically more beneficial, it would be preferable to have an annual production of 100,000-500,000 tonnes (Eerhart, *et al*., 2012). Ideally there would be a plant in Europe with the capacity to produce a minimum of 200,000 tonnes of FDCA per year (The PEFerence Project Group, 2017-2018).

2.5 PEF – A Substitute to PET

PEF is a transparent bioplastics that has proven to exhibit better gas barrier characteristics than PET. It contains oxygen ten times better and carbon dioxide six-ten times better than PET, but also water two times better (Avantium, 2020), which is why PEF would be a suitable substitute for PET in soft drink bottles. It also exhibits better mechanical properties such as 60 % higher tensile modulus, meaning it is more durable (The PEFerence Project Group, 2017-2018). As a result of this, a thinner PEF layer is enough in bottles and packaging, leading to a decreased usage of resources (Avantium, 2020). According to the EU project PEFerence, the calculated cost price for the 100 % recyclable PEF suggests that it will challenge the commonly used aluminium cans, small PET bottles and certain types of multi-layered packaging. PEF do also withstand heat better than PET and this could be especially useful with filling bottles with hot contents. (The PEFerence Project Group, 2017-2018)

The production of PEF from FDCA can be performed at considerably lower temperature and at half the time, compared to PET production from polyterephthalic acid (PTA) (Eerhart, *et al.*, 2012), making it less energy consuming.

2.6 The PET Market

In total, 30.3 million tonnes of PET resin was globally produced in 2017. Europe stands for just under 15 % of this production with 4.45 million tonnes (Plastics Insight, 2019). PET is used solely in packaging (PlasticsEurope, 2019), such as fiber and film production, different soft drink bottles, cleaning products' bottles and various packing materials (Sajid, *et al.*, 2018).

In September 2017, PET resin was sold for 23,000 SEK/tonne when taking the average price in Belgium, France, Germany, Italy and UK. PET resin is the form it is sold as on the market, and is further transformed into melted PET and formed to desired shape (Plastics Insight, 2019).

2.7 Feedstock Limitations

Today's sugar production is not enough to support a sufficient PEF production. In order to have an adequate supply of sugar, the production would have to increase.

2.8 Recycling of PEF

Tests have shown that PEF is possible to be recycled with the current recycling systems. It is also easy to sort out PEF from PET by the use of optical techniques, which are already apart

of today’s recycling systems. (Avantium, 2020) This facilitates the introduction of PEF in everyday household items since no additional techniques or systems are needed.

3 Materials and Methods

In the upcoming sections the working method will be presented, which include assumptions that the results are based upon, a size determination of the process and simulations. For the simulations the modelling tool ASPEN Plus V10 has been used.

3.1 Assumptions

To be able to deliver an industrial scale process design, some assumptions had to be made. The assumptions made in the project are listed in Table 3.1.

Table 3.1. Summary of assumptions made throughout the report.

	Assumption
Operating time	Assuming there are 8000 operating hours per year.
Energy cost	Energy price is 0.60 SEK/kWh.
Currency conversion	December 31st 2019 gave a conversion rate of 1 USD is 9.37 SEK (Exchange-rates.org, 2020).
Tank volume	The liquid volume in the reactor tanks is 80 % of the total vessel volume.
Reactor 1	Mixing happens due to sparging with air.
Filter	- The filter retains 98 % of the FDCA. - Permeate flow consists of only water, sulphuric acid and 2 % FDCA. - The capacity of that filter is assumed to be half of the maximum capacity for the Vacuum drum filter YU from Andritz. - FDCA is assumed to form particles similar to the size of very fine sand particles (50-250 µm in diameter)
Precipitation of FDCA	- The sulphuric acid dissolves completely in the reaction mixture. - That 98 % pure sulphuric acid has the same density as completely pure sulphuric acid
Reactor 2	- The liquid in the tank have the characteristics of pure water. - The specific heat capacity is approximated to be 4.2 kJ/(kg*K).
Heat transfer	- Heat transfer coefficient is assumed to be 100 W/(K*m^2) (Hall, 2012). - For the heat exchange between streams, an efficiency of the heat transfer is assumed to be 70 %, due to some energy loss.
Flash	- A residence time of 5-10 minutes when the separator is half-full. - The flash unit operates without any energy requirement for the separation, but energy is needed to avoid cooling.
Enzyme cost	- The cost baseline for production of cellulase will be used. - The enzymes will be assumed to be recycled ten times.
Water	Municipal water is available at the production site.

3.2 Simulation Size Determination

When considering the desired amount of 200,000 tonnes of FDCA being produced in Europe per year, an estimation of the capacity for the process design can be done.

Assuming there are 8000 operating hours per year, 25 tonne/h needs to be produced in order to reach the desired amount of 200,000 tonnes FDCA per year. With a 100 % yield from HMF to FDCA, this means 21 tonne/h HMF is needed. The reaction in the simulation has a volume of 4800 m^3.

The required amount of sugar per year is estimated to be 500,000 tonne. This is more than what was assumed to be possible to use for this purpose, from the current sugar supply, and the current sugar production would need to increase in order to be sufficient. The production would need to increase with 20 %.

3.3 Flowsheet

For the primary flowsheet set-up, the reaction temperature was set to 100 °C and the pressure to 10 bar(a) (in reactor 1), as it was found in literature for a suitable process design (Bello, *et al.*, 2020). Once the simulation converged at these parameters, the conditions were changed into the tailored ones for the enzyme-catalysed reaction. A few units were also removed from the process design found in literature, since they were found to be unnecessary. The final flowsheet is depicted in Figure 3.1. For the simulation, the physical property method NRTL was chosen since it is suitable for liquid-liquid systems (Smith, 2016).

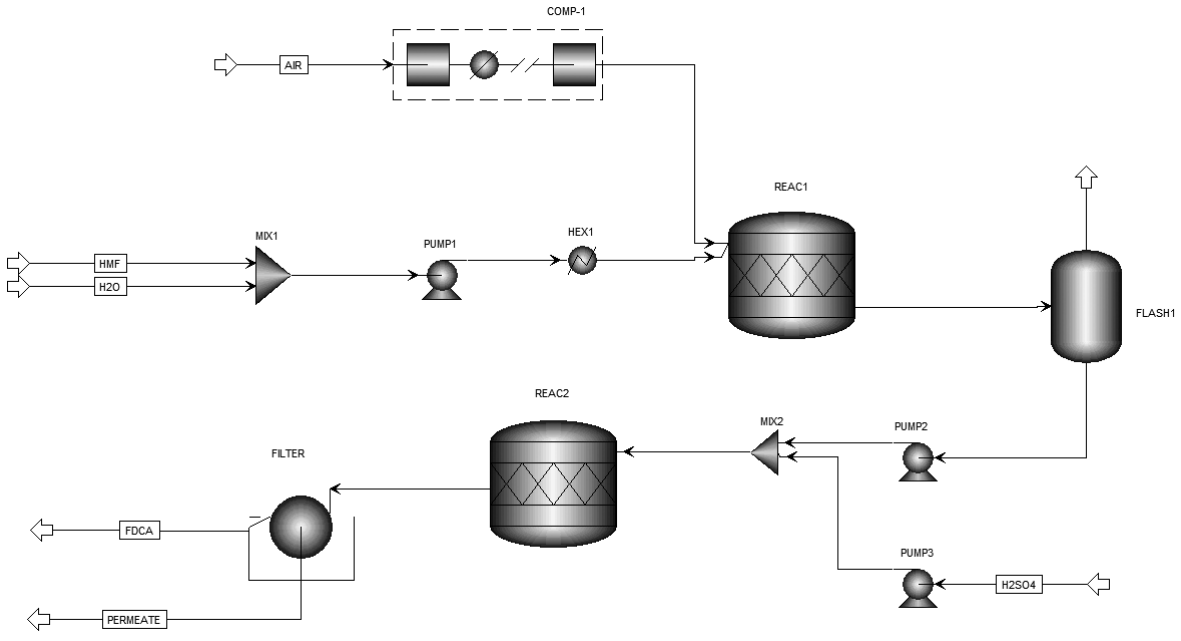


Figure 3.1. Flowsheet of the FDCA synthesis simulated in ASPEN Plus.

3.3.1 Reactor Type

The process is performed in a one-pot, continuous mode. In ASPEN Plus the chosen reactor type was RStoic. The reactor was set to perform the 100 % conversion of HMF and oxygen to FDCA and water.

The size of the reactor calculation was based on the assumption that the reaction mixture takes up 80 % of the reactor volume. The reactor volume is thereby determined to be 6000 m^3.

Reactor conditions
A pH of 7.0 in the reactor is the optimum for the HMF oxidation and the reaction temperature is 37 °C (McKenna, *et al*., 2017). The pressure in the reactor was calculated to be 4.9 bar(a).

3.3.2 Downstream Process
There are mainly two options for the separation of FDCA from the stream out from the reactor; crystallization/precipitation or distillation (Bello, *et al*., 2018). To reduce the energy use for the downstream process, it is favourable to precipitate the FDCA instead of using distillation (Bello, *et al*., 2020). However, the method requires that the pH of the reaction mixture is changed. This needs to be compensated for before possible recycling or waste treatment.

Removal of Excess Air
To separate the excess air that is dissolved in the outgoing stream of the reactor, a flash unit is added. The conditions in the flash are changed compared to those of the reactor in order to cause separation of air from the liquid. The flash is operated at 1.5 bar(a) and 30 °C.

Precipitation by Addition of Sulphuric Acid
To cause FDCA to precipitate, the reaction mixture can be acidified (McKenna, *et al*., 2017) to lower the pH below FDCA's pKa value. For this purpose, H_2SO_4 (Sajid, *et al*., 2018) will be added to the reactor located after the flash. This will result in a white precipitate.

FDCA has a pKa value of 2.3-3.5 (ECHA, 2019); therefore the pH should be lowered to below 2.3 to ensure good precipitation. Enough sulphuric acid will be added to adjust the pH to 2.0 for this purpose.

Filtration and Drying of FDCA
To separate the precipitated FDCA from the liquid stream, a filter is used. The filter will retain the FDCA particles and allow the liquid to pass through. For this purpose, a rotary vacuum filter is used and 98 % wt. of the FDCA is retrieved in the filter cake (Bello, *et al*., 2020).

4 Results

The findings of the project will be presented and summarized in the following sections. First, the chosen equipment will be described, together with the required size and the bare module cost. Next, the amounts and cost of the reagents used will be presented. Thereafter the utility consumption of the process design is presented. Finally, a cost analysis is done, including a sensitivity analysis of the two dominating costs and the overall cost of production will provide the cost per tonne for the production of FDCA.

4.1 Equipment – Type, Size and Cost

After the simulation was accomplished, an analysis was done of what was required to build the process design. An overview of the equipment can be seen in Table 4.1.

Table 4.1. An overview of the equipment, functions, specifications and construction material used for the final design.

Equipment	Function	Specification	Construction material
Pump 1	Pressurize the ingoing stream of reactants to the reactor.	Centrifugal pump with a shaft power of 3.6 kW. Section pressure of 0 bar(a). Pressurizes the stream to 4.9 bar(a).	Cast iron
Reactor 1	Mixes HMF solution with air, which reacts to form FDCA.	Eight plain reactor vessels with Bayonet Bundle of a vessel volume of 750 m^3 each. Operating pressure of 3.9 bar(g) and 37 °C. Coil surface area of 10,700 m^2 in total.	Vessel: Carbon steel Coil: Carbon steel
Compressor 1	Pressurize the ingoing air to the reactor.	A positive displacement rotary compressor with an energy requirement of 2170 kW. Outgoing stream is pressurized to 4.9 bar(a).	Carbon steel
Flash	Separate the excess air from the liquid stream.	A vertically oriented process vessel with mist elimination. Inside diameter is 2.6 m and the height 11.8 m. Total volume of 80 m^3. Operating pressure of 1.5 bar(a) and 30 °C.	Vessel: Carbon steel Mist eliminator: Stainless steel
Pump 2	Pressurize the ingoing stream of FDCA solution to the reactor	Centrifugal pump with a shaft power of 3.6 kW. Section pressure of 0 bar(a). Pressurizes the stream to 3 bar(a).	Cast iron
Pump 3	Pressurize the ingoing stream of sulphuric	Centrifugal pump with a shaft power of 0.04 kW. Section pressure of 0 bar(a). Pressurizes the stream to 3 bar(a).	Cast iron

	acid to the reactor		
Reactor 2	Mixes reaction mixture with sulphuric acid and the dissolved FDCA to precipitates.	Plain vessel, no coil with a total volume of 80 m^3. Operating pressure 1.5 bar(g) and temperature 15 °C.	Carbon steel
Filter	Separates the solid FDCA from the liquid stream.	Multi-compartment vacuum drum filter. 14 units of 35 m^2 each, where one is redundancy. Filter pore size is 50 µm. Drum rotates at 15 rpm.	Carbon steel

4.1.1 Reactor 1

The reactor volume required to produce 160 kmol FDCA per hour is 6000 m^3. Reactors of this size are not realistic. Using the tool EconExpert, it is found that using eight reactors of the size 750 m^3 each is feasible (Ulrich & Vasudevan, u.d.).

The estimated bare module cost is 35,840,000 SEK (Ulrich & Vasudevan, u.d.) for eight reactors with built-in heating. The reactors will in total have 24 coil units to accommodate the necessary heat transfer (Ulrich & Vasudevan, u.d.).

4.1.2 Pump 1, 2 and 3

Centrifugal pumps will be recommended for the process design since they are common in industry and are cheaper than positive displacement pumps (Smith, 2016, pp. 355-356). The total bare module cost for the three centrifugal pumps needed is 2,040,000 SEK.

Pump 1

The first pump is located before the reactor, to ensure the ingoing liquid is pressurized appropriately. The liquid leaving the pump will have a pressure of 4.9 bar(a). The bare module cost is 1,180,000 SEK (Ulrich & Vasudevan, u.d.).

Pump 2 and 3

The second and third pumps are both located before the precipitation tank, to adjust both liquid streams to 3 bar(a). However, the two pumps will handle two completely differently sized streams, hence they will have individual capacities and will therefore differ in cost. The bare module cost for pump 2 is 770,000 SEK and for pump 3 is 90,000 SEK (Ulrich & Vasudevan, u.d.).

4.1.3 Compressor

To compress the air to 4.9 bar(a) before feeding it to reactor 1, a compressor is need. The bare module cost for a positive displacement rotary compressor (twin-lube, rotary-screw, sliding vane compressor in EconExpert) is 24,960,000 SEK (Ulrich & Vasudevan, u.d.).

4.1.4 Flash

To perform the separation of the residual gas in the stream out of the reactor, a flash tank will be installed. This unit is called flash in the performed ASPEN simulation. For this purpose, a vertically oriented process vessel with mist elimination is chosen.

The size of the process vessel is determined by following the guidelines of optimal sizing of vapour-liquid separators (Hall, 2012). A summary of the found values can be seen in Table 4.2.

Table 4.2. Summary of gas-liquid separation vessel parameters

Parameter	Value
Diameter$_{vessel,\ min}$	2.6 m
Height of vessel	11.8 m
Diameter$_{nozzle}$	0.71 m
Vessel volume	62 m^3
Residence time	5-10 minutes

The bare module cost for a vertical vessel of this size would be 3,630,000 SEK (Ulrich & Vasudevan, u.d.). The separator is operating at 1.5 bar(a) and 30 °C. In Appendix 9.4 the calculations for the size determination can be found, together with an estimation of diameters of the outgoing pipes from the flash.

4.1.5 Reactor 2

To perform the precipitation of FDCA by addition of sulphuric acid, a reaction vessel is required. A reactor volume of 80 m^3 is found to be suitable.

A reactor of this size has a bare module cost of 950,000 SEK (Ulrich & Vasudevan, u.d.). Operating at 15°C and 2.5 bar(a).

4.1.6 Filter

To purify the precipitated FDCA from the liquid stream, a filter is required. Cake filtration, a filtration method where the particles is retrieved from the retentate is used. A rotary vacuum filter is chosen. The model chosen is the Vacuum drum filter from Andritz (2020). FDCA is assumed to form particles similar to the size of very fine sand particles (50-250 µm in diameter (Skaggs, *et al.*, 2001)). For this process, a filter with a pore size of 50 µm is selected.

In total 14 filter units are needed and that includes additional unit for redundancy. The bare module cost per unit is 3,100,000 SEK (Ulrich & Vasudevan, u.d.), which gives a total bare module cost for 14 filter units of 43,400,000 SEK. The bare module cost is estimated for a multi-compartment filter unit.

The Vacuum drum filter YU washes and dries the cake (Andritz Separation, 2020) so no additional drying facility is needed.

4.2 Reagents – Amounts and Cost

4.2.1 HMF

With an annual need of 161,600 tonnes of HMF, it means that about 3100 tonnes are needed per week. To find a representative market price for the purchase of HMF has shown to be difficult, since it varies greatly between different suppliers and whether they are located in Asia or Europe. Since such a large quantity is needed, it might be necessary to have several suppliers to have sufficient amounts. The cost used for the estimation is US$ 1000-2000/tonne (Alibaba.com, 2020). A mean price of US$ 1500/tonne is used in the calculations. The annual cost for HMF is 2271 MSEK.

4.2.2 Enzymes

For the industrial scale production, a reaction mixture of 800,820 L/h is needed and the amounts of each enzyme was calculated and listed in Table 4.3. The concentrations are based on findings in the literature review (McKenna, *et al*., 2017). The amounts are given in kg/h and do not take any recycling into account.

Table 4.3. The enzymes needed for the FDCA production, given in concentration and the required amounts for an industrial scale production, without any recycle.

Enzyme	Concentration in reaction mixture (g/L)	Amount of enzyme (kg/h)
PaoABC	28.9	23,144
GOase M3-5	3.0	2402
Catalase	3.3	2643
HRP	1.0	801
Total		28,990

The Cost of Using Enzymes

It is difficult to determine exactly how much enzyme is needed for the annual production. Promising research has been done on immobilization of enzymes for this purpose, without loss of performance. This would, as mentioned in section 2.3.1, reduce the amounts used since recycling of the enzymes seem to be possible up to 14 times *(McKenna, et al.*, 2017). Even if just basing the estimations on a recycling of ten times, it would cut the costs greatly.

Enzymes do usually stand for a large share of the total cost of bio-produced compounds. To get an idea of how much of the total cost that comes from enzymes, the bio-production of lignocellulosic ethanol will be observed, mainly because it is commonly researched and discussed in literature (Klein-Marcuschamer, *et al.*, 2012), while not many other are.

When producing cellulase, used in the production of lignocellulosic ethanol, it has shown that almost half of the annual operating cost has to do with capital investment and around one third comes from raw material costs. The cost baseline for the production is stated to be US$ 10.14/kg. (Klein-Marcuschamer, *et al.*, 2012)

To get an approximation of the cost of enzymes, the cost baseline for production of cellulase will be used, and the enzymes will be assumed to be recycled ten times. The assumption is made that the amount of enzymes needed for the catalysis, can be combined, and thereby not distinguish the separate amounts, to be able to do the cost approximation. This is probably a

big simplification, but due to a lot of uncertainty in enzyme-related costs it is believed to be necessary. It would result in an annual minimum cost for the enzymes of 2204 MSEK.

4.2.3 Sulphuric Acid and Sodium Hydroxide

To adjust the pH in the process, sulphuric acid (H_2SO_4) is added in the precipitation step to lower the pH below the pKa value of FDCA. Sodium hydroxide (NaOH) will be added to increase the pH again after the precipitation step, to enable recycling of the liquid stream, and/or neutralize the pH to facilitate waste handling. This means there is an annual requirement of 3329 tonnes of sulphuric acid and 2715 tonnes of sodium hydroxide. The annual cost is 3 MSEK for sulphuric acid and 14 MSEK for sodium hydroxide (ICIS, 2020).

4.3 Economic assessment

In the following sections the components of the economic analysis will be presented. These include the capital cost, the operating cost and the overall cost of production. A sensitivity analysis of the biggest cost categories is also specified. The method used for the economic analysis is the Ulrich method (Ulrich & Vasudevan, 2004), which the following sections will be based upon. A plant lifetime of ten years is assumed.

4.3.1 Capital Cost

The capital cost can be divided into two subcategories; *investment cost* and *fixed capital cost*. The total capital cost is 95 MSEK.

Investment Cost

Grass root cost, or investment cost, is given by multiplying the total bare module cost with two auxiliary facilities-factors, the factors are found in Appendix 9.8.1, and the annuity factor. This results in a grass root cost of 21 MSEK per year. The bare module cost of the equipment can be seen in Table 4.4.

Table 4.4. Overview of the bare module cost for the total process design and for each equipment type (Ulrich & Vasudevan, u.d.).

Unit	Bare module cost (SEK)
Pump 1	1,180,000
Reactor 1	35,840,000
Compressor 1	24,960,000
Flash	3,630,000
Pump 2	770,000
Pump 3	90,000
Reactor 2	950,000
Filter	43,400,000
Total cost	110,820,000

Fixed Capital Cost

Storage of feedstock, storage of product and spare parts for the equipment are all a part of the fixed capital cost. The feedstock, HMF, is assumed to have a storage time of 16 days, which is the median number of days when applying the rule of thumb. The same method is followed when estimating a storage time for the FDCA of 31 days. (Ulrich & Vasudevan, 2004)

The annual cost for the storage is calculated to be 13 MSEK for the feedstock and 61 MSEK for the product, leading to a total storage cost of 74 MSEK. The cost for spare parts is assumed to be 15 % of the maintenance and repair costs (Ulrich & Vasudevan, 2004) (section 4.3.2) which results in 200,000 SEK The cost for spare parts are very low and will be neglected in the total cost.

4.3.2 Operating Cost

The operating cost can be divided into *direct cost* and *indirect cost*. The total operating cost is 4772 MSEK.

Direct Cost

In the direct cost, the cost of feedstock and other reagents is included, as well as maintenance and repair, operators and supervisors and utility consumption. The total direct cost is 4765 MSEK.

The total annual cost for the feedstock and reagents is 4492 MSEK. This, together with the respective costs, can be seen in Table 4.5.

Table 4.5. Summary of the reagents used in the FDCA synthesis showing annual need, cost per tonne and the annual cost for the separate categories and the total.

	Annual need (tonne)	**Cost (SEK/tonne)**	**Annual cost (MSEK)**	**Reference**
HMF	161,586	14,055	2271	(Alibaba.com, 2020)
H_2SO_4	3329	920	3	(ICIS, 2020)
NaOH	2715	5170	14	(ICIS, 2020)
Enzymes	23,192	95,012	2204	(Klein-Marcuschamer, *et al*., 2012)
Total	-	-	4492	

The cost for maintenance and repair is estimated to be 1 MSEK, which is 6 % of the grass roots cost (Ulrich & Vasudevan, 2004).

To run the production facility, the number of operators needs to be estimated. It is found that five operators are needed, and the production is run in five-shift. The cost for having five operators in five-shift production is 9 MSEK per year. A cost of 15 % on operators' costs is added to cover supervisors, which adds an extra 1 MSEK. (Ulrich & Vasudevan, 2004)

In Table 4.6 the utility consumption can be seen, which includes the net energy consumption, the annual consumption and the resulting cost of approximately 112 MSEK, based on an electricity price of 0.60 SEK/kWh. Almost 60 % of the required energy is used for heating in reactor 1. The origins of the requirements and estimations for each unit operation are found in Appendix 9.8.2.

Table 4.6. Net energy consumption for all unit operations and the annual energy requirement together with the respective costs.

Unit	**Net Energy Requirement (kW)**	**Annual Energy Requirement (kWh)**	**Cost (SEK)**
Reactor 1	13,850	110,800,000	66,480,000
Pump 1	100	800,000	480,000

Compressor 1	2170	17,360,000	10,419,000
Flash	6410	51,280,000	30,786,000
Pump 2	40	320,000	192,000
Reactor 2	60	480,000	288,000
Filter	630	5,040,000	3,024,000
Total	23,260	186,168,500	111,648,000

Water is used to get a tolerable HMF concentration for the enzymes. The cost for the water needed in the production have to be added. With a cost of 23.82 SEK/m^3 (VASYD, 2020) the annual cost for water is found to be 150 MSEK. It is assumed that the municipal water is available at the plant area.

Indirect Cost

Total indirect costs, consisting of cost overhead and cost for administration, are 8 MSEK per year. Cost overhead for staff is estimated to be 70 % on operators, resulting in 6 MSEK per year. Cost for administration is assumed to be 25 % on staff overhead, which equals to 2 MSEK per year. It is assumed that distribution and sales, as well as R&D, are zero for this production. Cost for licences and fees are also set to zero. Operating personnel is assumed to perform the lab work required.

4.3.3 Overall Cost of Production

The overall cost of production is the sum of the operating cost and capital cost. The cost estimations made in the economic analysis are summarized in Table 4.7.

Table 4.7. Overall annual cost for the FDCA production, including both capital cost and operating cost in SEK.

	Cost (MSEK)
Capital cost	
- **Storage of feedstock**	13
- **Storage of product**	61
- **Grass root cost**	21
Total capital cost	***95***
Operating cost (direct cost)	
- **Feedstock**	2271
- **Reagents**	2221
- **Electricity**	112
- **Water**	150
- **Maintenance and repair**	1
- **Operators**	9
- **Supervisors**	1
Total	***4765***
Operating cost (indirect cost)	
- **Overhead for staff**	6
- **Administration**	2
Total	***8***
Total operating cost	***4772***
Total cost	***4868***

There is a total annual cost for the FDCA production of 4868 MSEK, which gives a cost of 24,300 SEK/tonne. This is also the break-even price, when cost and income would be the same. In Figure 4.1 it can be seen that the cost of feedstock and cost of other reagents are dominating in the overall cost of production. The cost of HMF is 47 % and the cost of enzymes is 45 % out of the total overall costs. To see how the overall cost can vary, a sensitivity analysis of feedstock cost and reagent cost is done.

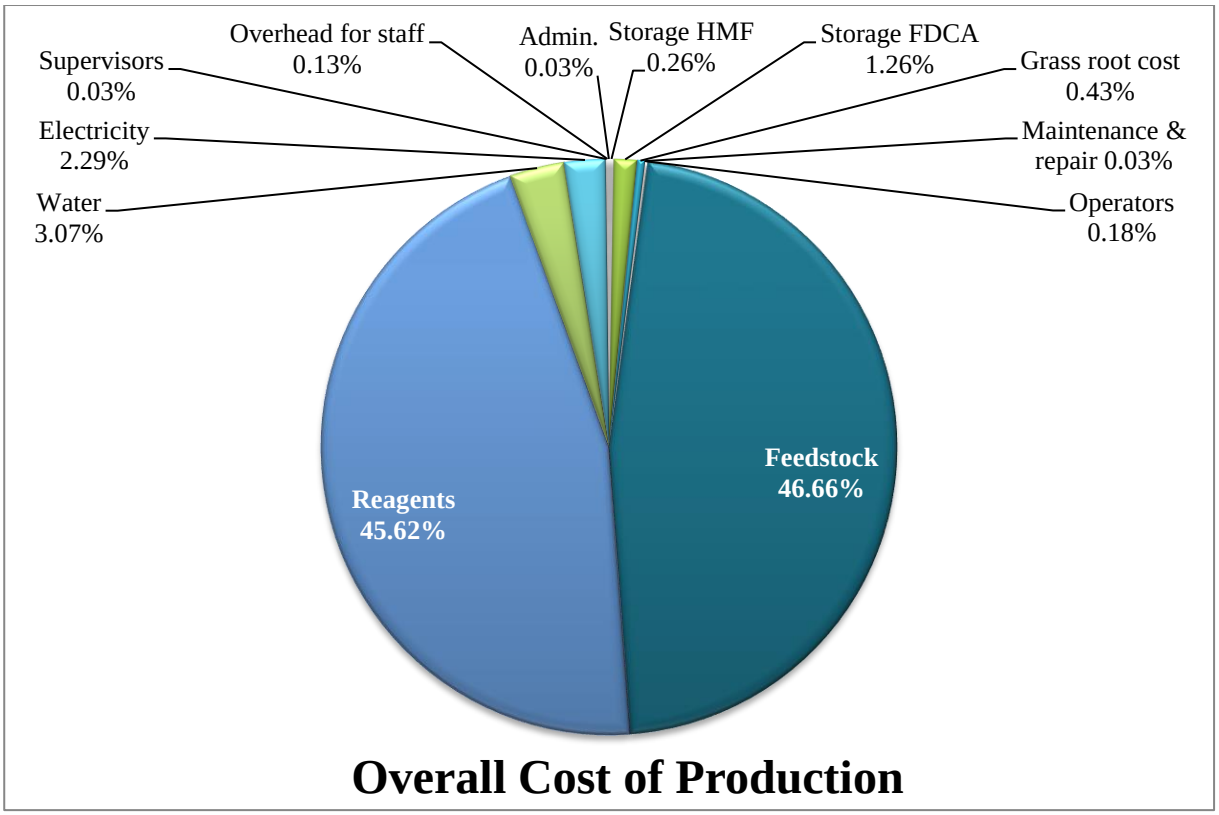


Figure 4.1. Pie chart showing the overall cost of production of FDCA.

Sensitivity Analysis

As stated before, the cost of feedstock and other reagents take up the largest share in the overall costs.

First, a sensitivity analysis is done on the feedstock cost. The price at which HMF is bought at, is investigated in two scenarios; one where it is reduced to half and one where it is doubled, compared to the estimated price of 14,055 SEK/tonne. The resulting price range of HMF is 1136-4542 MSEK per year.

In the same manner, the reagent cost is examined. When looking at a price reduced to half and when it is doubled, compared to the cost of all reagents of 2221 MSEK/year, the cost range is found to be 1110-4441 MSEK for the annual need.

In the case where the price of both the feedstock and the reagents is reduced to half, it results in an overall cost of production of 2621 MSEK, and a cost of 13,100 SEK/tonne. The worst-case scenario, when the price of feedstock and of reagents, are both doubled, it leads to an overall production cost of 9359 MSEK and the corresponding cost of 46,800 SEK/tonne.

4.3.4 Minimum Selling Price of FDCA

To get an estimation of what the price of FDCA could be, different payback scenarios are observed. The equation for payback time was written on the linear form seen in Equation 3. The payback time was then plotted towards the selling price of FDCA to give Figure 4.2.

$$Selling\ price\ FDCA = \frac{Grass\ roots\ cost}{Payback\ time} + Operating\ cost \quad (3)$$

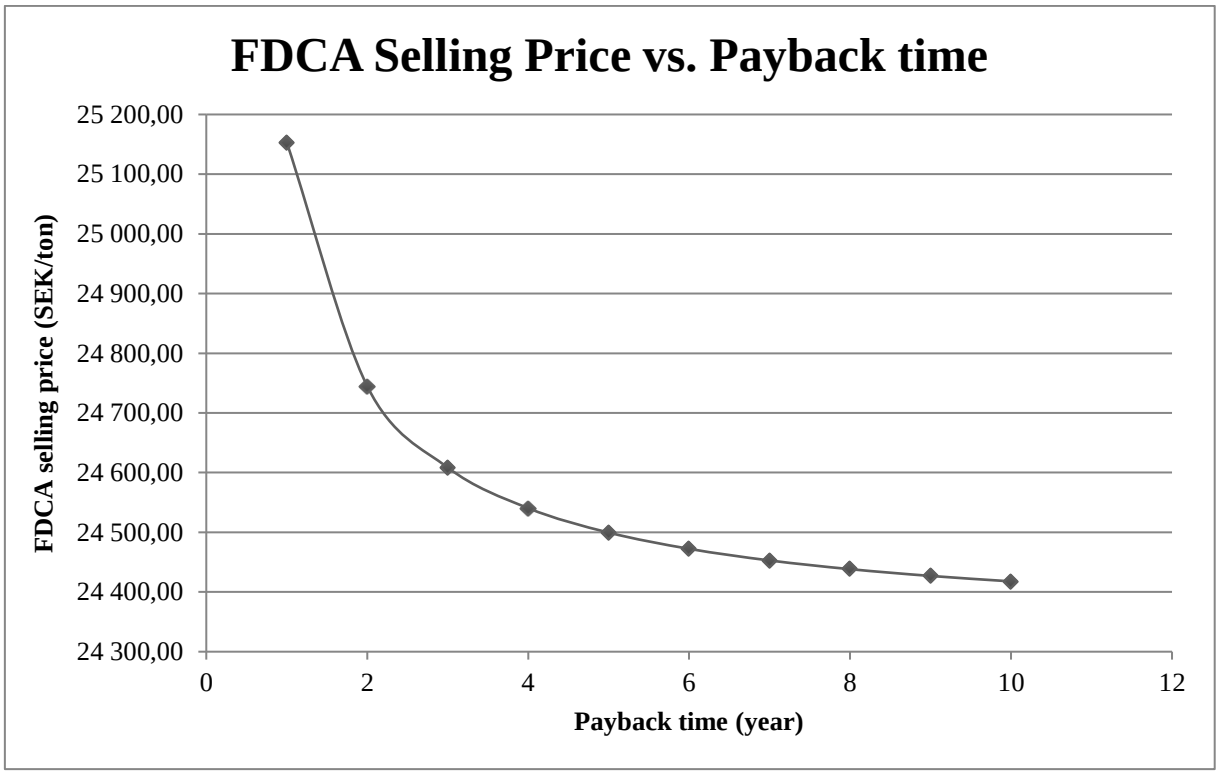


Figure 4.2. Plot of the minimum selling price of FDCA versus the payback time.

In Figure 4.2 it can be seen that the selling price of FDCA differs very little when the payback time varies between 1-10 years. The selling price only varies between 24,400-25,200 SEK/tonne, and should be seen as the minimum selling price. This indicates, as can be seen in Equation 3 too, that the operating cost is the factor affecting the selling price, and the potential profit, of FDCA the most.

4.3.5 Potential PEF Pricing

Looking at the PET resin prices of 23,000 SEK/tonne (section 2.6), it can be used to estimate the price that PEF can have to be competitive on the market. With the assumption that PEF can substitute PET with a 70:100 ratio, it allows a PEF price of 33,000 SEK/tonne. This is based on the fact that PEF has more desirable properties than PET. See section 2.5 for a more detailed comparison.

5 Discussion

The final process design is fairly simple regarding the type of equipment and the number of units needed. One reason behind the short downstream process is the full conversion of HMF to FDCA and the lack of by-products. Furthermore, the operating conditions are mild due the use of enzymes. The low pressure that is used does also contribute to a safer process environment.

The enzymes are assumed to be recycled ten times, without loss of efficiency. The recycling however, is not included in the simulation. To enable recycling of the permeate stream, the reaction mixture has to be purged to avoid build-up. The amounts of added sulphuric acid and sodium hydroxide will affect the volume of the liquid stream, and so will the precipitation of FDCA do too. This is an area that is believed to be necessary to investigate further before implementing. Introducing recycling would be a good way to be more environmentally friendly and to reduce the operating cost; it might however contribute to an increased grass root cost. Using immobilized enzymes would facilitate the recycling, but more research has to be done before this seem to be possible. With immobilized enzymes in the reactor, less consideration about the risk to damage of the enzymes would need to be taken during choice of equipment in the downstream process.

When looking at the economic assessment, it is reasonable to say that in order to reduce the cost of FDCA production, more research needs to be done regarding HMF and enzyme production. The cost of HMF and enzymes is the main contributor to the production cost. With more effort put into building more robust production systems for the two, the price could probably be lowered and assist FDCA in the competition with the fossil-derived PTA. However, a more thorough comparison of the HMF market could contribute to a more accurate estimation of the resulting cost. Another aspect that would increase the reliability of the economic assessment is the cost of enzymes. These were very roughly assumed to be representable by the price estimations of cellulase found in literature. A reason for this assumption is that it was difficult to find any enzyme prices from any distributors. What can be said from the estimation of the enzyme cost though, is that it is expensive and will affect the overall cost of production a lot, the question is exactly how much?

The electricity consumption is about 2 % of the overall cost of production, 112 MSEK annually, and more than half of this is consumed by the heating in reactor 1. A way to reduce this cost could be to use other energy sources such as steam. It would however only affect the total cost of production very little.

The market price of FDCA is another thing that is needed in order to make a proper economic analysis. To get a market price, that is compatible with that of PTA, the ratio PEF:PET that is required in the making of plastic product must be determined. It is known that PEF exhibits better properties than PET, but *how much* better it is might depend on the end use and the quality requirements. When that is determined, it would facilitate the setting of a FDCA market price, which in its turn would offer the possibility to make an estimation of the profit. The conversion of FDCA into PEF also needs to be further investigated for this purpose.

What was seen in the sensitivity analysis is that the cost of feedstock and other reagents will affect the production cost of FDCA greatly. To be able to determine a limit of how big of a price increase that is tolerable, some kind of minimum selling price of FDCA is needed. A

suggested minimum selling price is suggested based on the payback time of the investment. The sensitivity analysis resulted in a FDCA production cost range of 13,100-46,800 SEK/tonne. The upper part of this range is not believed to be tolerable, if comparing to the estimated market price of PEF (33,000 SEK/tonne). As stated above though, further research is needed in the area.

The minimum selling price that is suggested when plotting the minimum selling price versus the payback time in years is in the fairly narrow range 24,400-25,200 SEK/tonne. This further supports the claim that the operating cost, especially the cost of enzymes and HMF, should be the focus area regarding improvements. The payback time should be kept low in order to attract investors, while still having a FDCA selling price that ensures profitability.

6 Conclusions

The production volume was set in accordance with the request of the EU project PEFerence, and the plant size was determined thereafter. The performed process simulation resulted in a simplified and suitable final design for an annual FDCA production of 200,000 tonnes. The equipment is chosen to support a continuous production and the capital cost is estimated to be 95 MSEK. The operating cost is found to be 4772 MSEK per year, where the cost for HMF and enzymes stands for a large share.

7 Future Work

As discussed in section 0, the cost of feedstock as well as the cost of enzymes needs to be further researched and lowered in order to reduce the production cost of FDCA. The use of PaoABC, GOase $M_{3-5,}$ HRP and catalase as catalysts should probably be tested on a larger scale than only lab-scale, before introducing them in industrial scale production, to validate the amounts needed. This is considered to be crucial to ensure successful conversion of HMF to FDCA when scale-up is done. Doing this could potentially affect the enzyme cost, hopefully leading to a reduction.

Another area that should be examined is the market price of FDCA and of PEF. These need to be investigated further in order to get a full economic assessment of the FDCA production.

8 Reference list

Alibaba.com, 2020. *Alibaba.com.* [Online]
Available at: https://www.alibaba.com/
[Accessed 31 March 2020].

Alveteg, M., 2020. *Handbook: Physical properties, correlations and equations.* 2020 ed. Lund: Department of Chemical Engineering, Faculty of Engineering, Lund University.

Andritz Separation, 2020. *Andritz - Vacuum drum filter YU.* [Online]
Available at: https://www.andritz.com/products-en/group/separation/disc-drum-filters/vacuum-drum-filter-yu
[Accessed 07 05 2020].

Avantium, 2020. *Avantium: YXY Technology.* [Online]
Available at: https://www.avantium.com/technologies/yxy/
[Accessed 26 February 2020].

Bello, S. et al., 2020. Towards improving the sustainability of bioplastics: Process modelling and life cycle assessment of two separation routes for 2,5-furandicarboxylic acid. *Separation and Purification Technology,* Volume 233.

Bello, S. et al., 2018. Environmental sustainability assessment of HMF and FDCA production from lignocellulosic biomass through life cycle assessment (LCA). *Holzforschung,* 73(1), pp. 105-115.

Cao, L., van Langen, L. & Sheldon, R. A., 2003. Immobilised enzymes: carrier-bound or carrier-free?. *Current Opinion in Biotechnology,* 14(4), pp. 387-394.

Chen, G., van Straalen, N. M. & Roelofs, D., 2016. The ecotoxicogenomic assessment of soil toxicity associated with the production chain of 2,5-furandicarboxylic acid (FDCA), a candidate bio-based green chemical building block. *Green Chem.,* Volume 18, pp. 4420-4431.

Chheda, J. N., Román-Leshkov, Y. & Dumesic, J. A., 2007. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.,* Volume 9, pp. 342-350.

Dijkman, W. P., Groothius, D. E. & Fraaije, M. W., 2014. Enzyme-Catalyzed Oxidation of 5-Hydroxymethylfurfural to Furan-2,5-dicarboxylic Acid. *Angew. Chem. Int. Ed.,* Volume 53, pp. 6515-6518.

ECHA, 2019. *ECHA: European Chemicals Agency Substance Infocard Furan 2,5-dicarboxylic acid.* [Online]
Available at: https://echa.europa.eu/substance-information/-/substanceinfo/100.019.819
[Accessed 27 March 2020].

Eerhart, A. J. J. E., Faaij, A. P. C. & Patel, M. K., 2012. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ. Sci.,* Volume 5, pp. 6407-6422.

Exchange-rates.org, 2020. *Exchange-rates.org.* [Online]
Available at: https://www.exchange-rates.org/Rate/USD/SEK/12-31-2019
[Accessed 14 May 2020].

Fang, Z., Smith, J. R. L. & Qi, X., 2017. *Biofuels and Biorefineries Volume 7: Production of Platform Chemicals from Sustainable Resources.* Singapore: Springer Nature.

Hall, S., 2012. *Rules of Thumb for Chemical Engineers.* 5th ed. Oxford, UK: Elsevier Inc..

ICIS, 2020. *ICIS: Independent Commodity Intellegence Services.* [Online]
Available at: ICIS.com
[Accessed 2 April 2020].

Klein-Marcuschamer, D., Oleskowicz-Popiel, P. & Simmons, B. A., 2012. The challenge of enzyme cost in the production of lignocellulosic biofuels. *Biotechnology and Bioengineering,* 109(4), pp. 1083-1087.

Körner, P., Jung, D. & Kruse, A., 2018. The effect of different Brønsted acids on the hydrothermal conversion of fructose to HMF. *Green Chem.,* Volume 20, pp. 2231-2241.

Martínez, I., 2020. *HEAT OF SOLUTION DATA FOR AQUEOUS SOLUTIONS.* [Online]
Available at: http://webserver.dmt.upm.es/~isidoro/dat1/Heat%20of%20solution%20data.pdf
[Accessed 18 May 2020].

McKenna, S. M. et al., 2017. The continuous oxidation of HMF to FDCA and the immobilisation and stabilisation of periplasmic aldehyde oxidase (PaoABC). *Green Chem.,* Volume 19, pp. 4660-4665.

Nordzucker AG, 2017/2018. *Future created in dialogue,* Braunschweig: Nordzucker AG.

Plastics Insight, 2019. *Plastics Insight: Polyethylene Terephthalate (PET): Production, Price, Market and its Properties.* [Online]
Available at: www.plasticsinsight.com/resin-intelligence/resin-prices/polyethylene-terephthalate/
[Accessed 5 February 2020].

PlasticsEurope, 2019. *Plastics – the Facts 2019: An analysis of European plastics production, demand and waste data,* s.l.: PlasticsEurope Deutschland e. V. and Messe Düsseldorf.

Sajid, M., Zhao, X. & Liu, D., 2018. Production of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF): recent progress focusing on chemical-catalytic routes. *Green Chem.,* Volume 20, pp. 5427-5453.

Skaggs, T. H., Arya, L. M., Shouse, P. J. & Mohanty, B. P., 2001. Estimating Particle-Size Distribution from Limited Soil Texture Data. *Soil Sci. Soc. Am. J.,* 65(4), pp. 1038-1044.

Smith, R., 2016. *Chemical process design and integration.* 2nd ed. Chichester: John Wiley & Sons Inc..

The PEFerence Project Group, 2017-2018. *PEFerence.* [Online]
Available at: https://peference.eu/
[Accessed 26 February 2020].

Ulrich, G. D. & Vasudevan, P. T., 2004. *Chemical Engineering Process Design and Economics: A Practical Guide.* Second ed. Durham, NH, USA: Process Publishing.

Ulrich, G. & Vasudevan, P. T., n.d. *EconExpert.* [Online]
Available at: http://ulrichvasudesign.com/econ.html
[Accessed 2 April 2020].

VASYD, 2020. *Avgifter för dricks- och avloppsvatten för villor i Eslövs kommun.* [Online]
Available at: https://www.vasyd.se/-/media/Documents/Informationsmaterial/Avgifter-vatten-och-avlopp/Eslov/Frenklad_Eslv-2020.pdf
[Accessed 31 May 2020].

Werpy, T. & Petersen, G., 2004. *Top Value Added Chemicals From Biomass Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas* , Oak Ridge: U.S. Department of Energy.

Yuan, H. et al., 2020. Biocatalytic production of 2,5-furandicarboxylic acid: recent advances and future perspectives. *Appl. Microbiol. Biotechnol.,* Volume 104, pp. 527-543.

Zhang, Z. & Deng, K., 2015. Recent Advances in the Catalytic Synthesis of 2,5-Furandicarboxylic Acid and Its Derivatives. *ACS Catal.,* 5(11), pp. 6529-6544.

9 Appendices

In the table below, some molecular weights and densities are shown. These have been used for calculations in the project.

Table 9.1. Chemical data used for calculations.

Parameter	FDCA	HMF	H_2O	H_2SO_4
Molecular weight (kg/kmol)	156.09	126.11	18.02	
Density (kg/L)	1.604	1.29	1	1.83

9.1 The PET Market

The PET price was based on an average of the prices in five European countries in 2017. Table 9.2 shows the respective prices, together with the average price.

Table 9.2. The PET price of 2017 in Belgium, France, Germany, Italy and UK in US$/tonne (Plastics Insight, 2019) and the corresponding price in SEK/tonne.

Country	US$/tonne	SEK/tonne
Belgium	3200	30,000
France	2900	27,000
Germany	2600	24,000
Italy	2500	23,000
UK	1300	12,000
Average	2500	23,200

9.2 Simulation Size Determination

The size determination is based on an annual production of 200,000 tonnes.

$$\frac{200{,}000{,}000\ kg\ FDCA/year}{156.09\ kg/kmol * 8000\ h/year} = 160.16\ kmol\ FDCA/h \rightarrow 160.16\ kmol\ HMF/h$$

$$m_{HMF} = 160.16\ kmol/h * 126.11\ kg/kmol = 20{,}198\ kg/h$$

The HMF concentration is 200 mM, which is used to determine the total flow into the reactor.

$$0.2\ mol/l = \frac{160.16\ kmol/h}{Volumetric\ flow} \rightarrow Volumetric\ flow = 800{,}820\ L/h$$

By approximating the density of the total flow to be the same as for water, it gives a mass flow of:

$$m_{total\ flow} = 800{,}820\ L/h * 1\ kg/L = 800{,}820\ kg/h$$

$$\frac{m_{HMF}}{m_{total\ flow}} = \frac{20{,}198\ kg/h}{800{,}820\ kg/h} * 100\ \% = 2.5\ \%$$

Since the HMF is only 2.5 % of the total mass flow, the stream will be approximated to the characteristics of pure water.

$$V_{R_{ASPEN}} = 800{,}820\ L/h * 6\ h = 4805\ m^3$$

Where $V_{R\ ASPEN}$ is the volume of the reaction mixture based on the amounts in the simulation in APSEN.

9.2.1 Sugar Demand

To calculate the amount of sucrose needed to fulfil the annual need of 200,000 tonnes FDCA, some conversions have to be done.

$$\frac{200{,}000{,}000\ kg/year}{156.09\ kg/kmol} = 1{,}281{,}312\ kmol\ FDCA/year$$

With a 100 % yield of FDCA from HMF, the same amount of HMF is required; 1,281,312 kmol HMF/year. The reaction from sucrose to HMF has a yield of 88.2 %, which means:

$$\frac{1{,}281{,}312\ kmol\ HMF/year}{0.882\ kmol\ HMF/kmol\ sucrose} = 1{,}452{,}735\ kmol\ sucrose/year$$

$$1{,}452{,}735\ \ kmol/year * 342.3\ \ kg/kmol = 497{,}271\ tonnes\ sucrose/year$$

The required amount of sugar per year is estimated to be 500,000 tonne. This is more than what was assumed to be possible to use for this purpose, from the current sugar production and the current sugar supply would need to increase in order to be sufficient. The production would need to increase with 20 %.

$$\frac{500{,}000\ tonnes}{2{,}500{,}000\ tonnes} * 100\ \% = 20\ \%$$

9.3 Reactor 1

9.3.1 Size

The size of the reactor calculation was based on the assumption that the reaction mixture takes up 80 % of the reactor volume. The reactor volume is thereby determined to be 6,006 m^3.

$$V_{reactor_{ASPEN}} = 1.25 * V_{R_{ASPEN}} = 6006\ m^3$$

9.3.2 Pressure

The ideal gas law, Equation 4, was used to calculate the pressure needed in the reactor for the oxygen in the air to dissolve in the reaction mixture.

$$pV = nRT \tag{4}$$

$$p = \frac{n_{air}RT}{V_{reactor_{ASPEN}}}$$

Where n_{air} is the molar flow of air to the reactor, R is the gas constant 8.3145 J/(mol*K), T is the temperature in the reactor and $V_{R\ ASPEN}$ is the simulated reaction volume multiplied with a factor of 1.25 to account for the dead volume in the reactor.

To estimate the amount of air needed, the amount of oxygen can be determined from the stoichiometry of the reaction.

$$n_{O_2} = 1.5 * n_{HMF} = 1.5 * 160.16\ kmol/h = 240\ kmol/h$$

$$n_{air} = \frac{n_{O_2}}{21} * 100 = 1144\ kmol/h$$

$$p = \frac{1144\ kmol/h * R * 310.15\ K}{6006\ m^3} = 4.9\ bar$$

9.3.3 Cost

The reactors have built-in heating. When calculating the required surface area for the heating, Equation 5 was used:

$$Q = k * A * \Delta T \tag{5}$$

Where Q is the heat transfer, k is the heat transfer coefficient, A is the heat transfer surface area and ΔT is the temperature difference. The heat transfer is taken from heat exchanger 1 in the ASPEN simulation and is 28,891 kW, the temperature difference is 27 K (from 283.15 K to 310.15 K) and the heat transfer coefficient is assumed to be 100 W/(K*m^2).

$$A = \frac{Q}{k * \Delta T} = \frac{28{,}891\ \ kW}{100\ W/(K * m^2) * 27\ K} = 10{,}700\ m^2$$

The heat transfer surface area is found to be 10,700 m^2. The eight reactors will in total have 24 coil units to accommodate the necessary heat transfer (Ulrich & Vasudevan, u.d.).

9.4 Flash – Size

The size of the process vessel is determined by following the guidelines of optimal sizing of vapour-liquid separators (Hall, 2012).

First, the liquid surge volume is determined. A residence time of 5-10 minutes when the separator is half-full is assumed, in accordance with the guidelines. To calculate the volume of the reflux drum full, V_d, Equation 6 (Hall, 2012) was used:

$$V_d = 2F_4(F_1 + F_2)(L + F_3D) \tag{6}$$

Where L is the reflux to the separator, in this case it is 0, and D is the outgoing stream that is to undergo further downstream processing, in this case 3659 gal/min. The factors F_i are process control related factors, where F_1 = 0.5, F_2 =1, F_3 =2 and F_4 =1. The factors correspond to having flow ratio control with alarm and good labour, operating under good control and having a broad-mounted level recorder monitor. (Hall, 2012, pp. 158-159) This resulted in a volume of the reflux drum full, of 21,954 gal.

In the second step, the maximum velocity of the vapour, $U_{vapour,max}$, is estimated by using Equation 7-9 (Hall, 2012):

$$U_{vapor,max} = K_V \sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \quad (7)$$

$$K_V = exp(-1.94 - 0.815X - 0.179X^2 - 0.0124X^3 + 0.00039X^4 + 0.00026X^5) \quad (8)$$

$$X = ln\left(\frac{W_L}{W_V}\sqrt{\frac{\rho_v}{\rho_L}}\right) \quad (9)$$

Where W_L is the liquid flow rate, W_V is the vapour flow rate, ρ_v is the density of the vapour and ρ_L is the density of the liquid. The flow rates are 510.43 lb/s and 16.80 lb/s respectively, and the densities are 0.10 lb/ft^3 for the vapour and 62.61 lb/ft^3 for the liquid. The data are taken from the simulation in ASPEN. This resulted in a maximum velocity of the vapour of 3.05 ft/s.

$$X = ln\left(\frac{510.43\ lb/s}{16.80\ lb/s}\sqrt{\frac{0.10\ lb/ft^3}{62.61\ lb/ft^3}}\right) = 0.194 \rightarrow K_V = 0.122$$

$$U_{vapor,max} = 0.122\sqrt{\frac{62.61\ \text{lb/ft}^3 - 0.10\ \text{lb/ft}^3}{0.10\ \text{lb/ft}^3}} = 3.05\ ft/s$$

The third step is to estimate the minimum cross-sectional area of the vessel, and therefrom the diameter. For this purpose, Equation 10 and 11 (Hall, 2012) are applied.

$$Area_{vessel,min} = \frac{W_V}{\rho_v U_{vapour,max}} \quad 10$$

$$d_{vessel,min} = 2\sqrt{\frac{Area_{min}}{\pi}} \quad 11$$

The smallest diameter that can be used is 100 inches (2.55 m) to ensure the vapour velocity is below the maximum. To follow the standard size increments, a diameter of 102 inches is chosen, which equals 2.59 m. The chosen diameter resulted in a cross-sectional area of 681 ft^2.

$$Area_{vessel,min} = \frac{16.80\ \text{lb/s}}{0.10\ \text{lb/ft}^3 * 3.05\ ft/s} = 55.15\ ft^2 \rightarrow d_{vessel,min} = 8.38\ ft = 2.55\ m$$

$$Area_{vessel} = \pi * \left(\frac{55.15\ ft}{2}\right)^2 = 681\ ft^2$$

Next, an average density of the feed is to be approximated and Equation 12 is applied:

$$\rho_{mix} = \frac{W_V + W_L}{\left(\frac{W_V}{\rho_v}\right) + \left(\frac{W_L}{\rho_L}\right)} \quad 12$$

The average density was approximated to 2.99 lb/ft^3.

$$\rho_{mix} = \frac{16.80\ \text{lb/s} + 510.43\ \text{lb/s}}{\left(\frac{16.80\ \text{lb/s}}{0.10\ \text{lb/ft}^3}\right) + \left(\frac{510.43\ \text{lb/s}}{62.61\ \text{lb/ft}^3}\right)} = 2.99\ \text{lb/ft}^3$$

The average density was further used to estimate a range of inlet nozzle velocities by using Equation 13 and 14.

$$U_{nozzle,max} = \frac{100}{\sqrt{\rho_{mix}}} \quad (13)$$

$$U_{nozzle,min} = \frac{60}{\sqrt{\rho_{mix}}} \quad (14)$$

The range for the inlet nozzle velocities was found to be 34.7-57.8 ft/s. This is further used to determine the equivalent sizes of the nozzles, see Equation 15. The nozzle should be in the range of 23.6-30.5 inches (60-78 cm) in diameter. A nozzle diameter of 28 inches (0.71 m) is chosen for further calculations.

$$U_{nozzle,max} = \frac{100}{\sqrt{2.99\ lb/ft^3}} = 57.8\ ft/s$$

$$U_{nozzle,min} = \frac{60}{\sqrt{2.99\ lb/ft^3}} = 34.7\ ft/s$$

$$Area_{nozzle} = \frac{W_V + W_L}{\rho_{mix} U_{nozzle}} \quad (15)$$

$$Area_{nozzle,min} = \frac{16.80\ \text{lb/s} + 510.43\ \text{lb/s}}{2.99\ \text{lb/ft}^3 * 57.8\ \text{ft/s}} = 3.05\ ft^2$$

$$\rightarrow d_{nozzle,min} = 2\sqrt{\frac{Area_{nozzle,min}}{\pi}} = 1.97\ ft = 23.6\ inch = 0.600\ m$$

$$Area_{nozzle,max} = \frac{16.80\ \text{lb/s} + 510.43\ \text{lb/s}}{2.99\ \text{lb/ft}^3 * 34.7\ \text{ft/s}} = 5.08\ ft^2$$

$$\rightarrow d_{nozzle,max} = 2\sqrt{\frac{Area_{nozzle,max}}{\pi}} = 2.54\ ft = 30.5\ inch = 0.770\ m$$

When estimating the final design of the vessel, Equation 16 is used for the height above the inlet nozzle plus half the inlet nozzle diameter (H_V), Equation 17 is used for the distance below the inlet nozzle to the high liquid level ($H_{in\text{-}liq}$) and the distance between the inlet nozzle and the bottom of the vessel have to be estimated (H_L).

By following guidelines (Hall, 2012), the

$$H_V = 36\ inch + \frac{d_{nozzle}}{2}\ or\ minimum\ 48\ inch \quad (16)$$

$$\mathrm{H_V} = 36\ \text{inch} + \frac{28\ inch}{2} = 50\ inch$$

$$H_{in-liq} = 12\ inch + \frac{d_{nozzle}}{2}\ or\ minimum\ 18\ inch \quad (17)$$

$$\mathrm{H_{in-liq}} = 12\ \mathrm{inch} + \frac{28\ inch}{2} = 26\ inch$$

$$H_L = \frac{V_d}{A_{vessel}} + H_{in-liq} = \frac{21{,}954\ gal}{681\ ft^2} + 26\ inch = 34.4\ ft = 413\ inch$$

$$H_{total} = H_V + H_L = \ 463\ inch = 11.76\ m$$

$$3 < \frac{H_{total}}{d_{vessel}} < 5$$

$$\frac{463\ inch}{102\ inch} = 4.5\ \rightarrow within\ range$$

To determine the size of the pipes out from the vessel, the volumetric flows were taken from the simulation. The gas stream out from the flash is 4.62 m^3/s and the liquid stream is 0.23 m^3/s. The rule of thumb for velocities of liquids and gases in pipes; 1.5-4 m/s and 15-40 m/s (Hall, 2012) respectively, gave the following dimensions:

$$Area_{cross} = \frac{Volumetric\ flow}{Velocity} \rightarrow d_{pipe} = 2\sqrt{\frac{Area_{cross}}{\pi}}$$

Where A_{cross} is the cross-sectional area of the pipes and d_{pipe} is the pipe diameter.

A gas stream of 15-40 m/s gives a pipe diameter of 38-63 cm.

$$A_{pipe_{15\ m/s}} = \frac{4.62\ m^3/s}{15\ m/s} = 0.31\ m^2 \rightarrow d_{pipe_{15\ m/s}} = 0.63\ m$$

$$A_{pipe_{40\ m/s}} = \frac{4.62\ m^3/s}{40\ m/s} = 0.12\ m^2 \rightarrow d_{pipe_{20\ m/s}} = 0.38\ m$$

A liquid stream of 1.5-4 m/s gives a pipe diameter of 27-44 cm.

$$A_{pipe_{1.5\ m/s}} = \frac{0.23\ m^3/s}{1.5\ m/s} = 0.15\ m^2 \rightarrow d_{pipe_{15\ m/s}} = 0.44\ m$$

$$A_{pipe_{4\ m/s}} = \frac{0.23\ m^3/s}{4\ m/s} = 0.06\ m^2 \rightarrow d_{pipe_{15\ m/s}} = 0.27\ m$$

9.5 Reactor 2 – Size

With a diameter (d_r) of 3.05 m and a height (h) of 10.97 m, it gives the vessel a volume of 80 m^3.

$$V_{precipitation\ vessel} = h * \left(\frac{d_r}{2}\right)^2 \pi = 10.97\ m * \left(\frac{3.05\ \mathrm{m}}{2}\right)^2 \pi = 80\ m^3$$

9.6 Filter – Size

To determine the size of the filter unit required for the process, the Vacuum drum filter YU (Andritz Separation, 2020) was chosen. The capacity of the filter can be seen in Table 9.3.

Table 9.3. Filter parameters for the chosen filter unit to separate the solid FDCA particles from the liquid stream.

Parameter	**Capacity of the Vacuum drum filter YU** (Andritz Separation, 2020)	**Estimated to be representative for the chosen filter**
$J_{membrane}$	Up to 4500 L/(m^2*h)	2250 L/(m^2*h)
Filter area	35 m^2	35 m^2
Filter particle sizes	50-300 µm	50 µm
Rotation speed$_{maximum}$	Up to 30 rpm	15 rpm

FDCA is assumed to form particles similar to the size of very fine sand particles (50-250 µm in diameter) (Skaggs, *et al.*, 2001). The ingoing stream to the filter unit taken from ASPEN Plus and is 831,391 L/h.

$$A_{membrane} = \frac{F_{total\ flow}}{J_{membrane}} = \frac{831{,}391\ L/h}{2250\ L/(m^2 * h)} = 370\ m^2$$

The required filter area is 370 m^2, but a safety margin is needed and an additional 20 % of filter area is therefore added. This results in a filter area of 444 m^2.

$$A_{membrane+20\,\%} = 1.2 * A_{membrane} = 444\ m^2$$

To see how many units of 35 m^2 each that are needed, and by adding an additional unit for redundancy and round up the number, it gives a total of 14 filter units.

$$No.of\ filter\ units = \frac{A_{membrane+20\,\%}}{35\ m^2/unit} + 1\ unit = 14\ units$$

9.7 Reagents – Amounts and Cost

9.7.1 HMF

The process requires 161,586 tonnes of HMF/year. The cost used for the estimation is US$ 1000-2000/tonne (Alibaba.com, 2020). A mean price of US$ 1500/tonne is used in the calculations.

$$Annual\ cost_{HMF} = US\$\ 1500 * 161{,}586\ tonnes = US\$\ 242.38M = 2271\ MSEK$$

9.7.2 Enzymes

The cost baseline for the production is stated to be US$ 10.14/kg (Klein-Marcuschamer, *et al.*, 2012).

$$Enzyme\ cost_{min} = \frac{m_{enzyme\ total}}{10\ recycles} * baseline\ production\ cost$$

$$Enzyme\ cost_{min} = \frac{28{,}990\ kg/h * 8000\ h}{10} * US\$\ 10.14/kg = MUS\$\ 235 = 2204\ MSEK$$

9.7.3 Sulphuric Acid and Sodium Hydroxide

The ingoing flow to the vessel is found from the ASPEN simulation and is 831,391 L/h.

$$C_{H_2SO_4} = \frac{0.98\ kg/kg}{98.08\ kg/kmol} * 1.83\ kg/L = 18.3\ mol/L$$

$$V_{liqiud_{in}} = 831{,}391\ L/h$$

$$C_{H^+ at\ pH\ 7.0} = 10^{-7}\ mol/L$$

$$C_{H^+ at\ pH\ 2.0} = 10^{-2}\ mol/L$$

$$\left(V_{liqiud_{in}} + V_{H_2SO_4}\right) * C_{H^+ at\ pH\ 2.0} - V_{liqiud_{in}} * C_{H^+ at\ pH\ 7.0} = 2 * V_{H_2SO_4} * C_{H_2SO_4} = 2 * n_{H_2SO_4}$$

$$\left(831{,}391\ L/h + V_{H_2SO_4}\right) * 10^{-2}\ mol/L - 831{,}391\ L/h * 10^{-7}\ mol/L = 2 * V_{H_2SO_4} * 18.3\ mol/L$$

$$\rightarrow V_{H_2SO_4} = 227.4\ L/h * 8{,}000\ h/year = 1{,}819{,}211\ L/year$$

$$m_{H_2SO_4} = 1{,}819{,}211\ L/year * 1.83\ kg/L = 3329\ tons/year$$

$$n_{H_2SO_4} = \frac{m_{H_2SO_4}}{M_{H_2SO_4}} = \frac{3329\ tons/year}{98.08\ kg/kmol} = 33{,}943\ kmol/year$$

$$\rightarrow n_{NaOH} = 2 * n_{H_2SO_4} = 2 * 33{,}943\ kmol/year = 67{,}886\ kmol/year$$

$$\rightarrow m_{NaOH} = 67{,}886\ kmol/year * 40\ kg/kmol = 2715\ tons\ NaOH/year$$

9.8 Economic Analysis

For the economic analysis the Ulrich method (Ulrich & Vasudevan, 2004) is used.

9.8.1 Capital Cost – Investment and Fixed Capital Costs

The annuity factor was estimated by the following calculations:

$$f_A = \frac{interest}{1 - (1 + interest)^{-plant\ life\ in\ years}}$$

The estimation of the interest is based on the assumption that 70 % of the required funding is lent on a bank with an interest of 2.5 %, and the other 30 % comes from investors with an interest of 10 %. This gives an average interest of 4.8 % for a plant lifetime of ten years.

$$Average\ interest = 0.7 * 2.5\ \% + 0.3 * 10\ \% = 4.8\ \%$$

$$f_A = \frac{0.048}{1 - (1 + 0.048)^{-10}} = 0.128$$

This factor was further used to calculate grass root cost and storage cost estimates.

The grass root cost is found to be approximately 21 MSEK. The factors 1.18 and 1.25 are used to account for auxiliary facilities. The annuity factor is also accounted for.

$$Grass\ root\ cost = 110{,}820{,}000\ SEK * 1.18 * 1.25 * 0.128 = 20{,}900{,}000\ SEK$$

$$Storage\ cost_{feedstock} = 161{,}586\ ton * f_A * 14{,}055\ SEK/ton * \frac{16}{365} = 12.7\ MSEK$$

To estimate the storage cost for the product, an estimation of the income from FDCA have to be done since FDCA is not commercially sold on the market yet. Since this estimation will only be used for storage cost, and in no other part of the economic assessment, the rough assumption is made that FDCA is sold for a price that is twice the price of HMF.

$$Storage\ cost_{product} = 200{,}000\ ton * f_A * 28{,}110\ SEK/ton * \frac{31}{365} = 61.1\ MSEK$$

To estimate cost of spare parts, the maintenance and repair cost (section 9.8.2) is used:

$$Spare\ parts = 0.15 * Maintenance\ and\ repair = 200{,}000\ SEK$$

$$Total\ capital\ cost = 21\ MSEK + 12.7\ MSEK + 61.1\ MSEK + 0.2\ MSEK = 95\ MSEK$$

9.8.2 Operating Cost – Direct and Indirect Costs

The direct and indirect costs adding up to the total operating cost of 4765 MSEK was calculated in accordance with the sections below.

The cost for maintenance and repair is estimated by the following calculation (Ulrich & Vasudevan, 2004):

$$Maintenance\ and\ repair\ cost = 0{,}06 * Grass\ root\ cost = 1.3\ MSEK$$

Numbers of operators where estimated by following the guidelines, see Table 9.4.

Table 9.4. Number of operators needed per unit in the plant. (Ulrich & Vasudevan, 2004)

Unit	**Reactor 1**	**Pumps**	**Compressor 1**	**Flash**	**Reactor 2**	**Filters**	**Mixers**
Number of units	8	3	1	1	1	14	1
Operators/unit	0.3	0	0.1	0.3	0.2	0.1	0.2
Total number of operators	4.6						

The cost for five operators in five-shift production is calculated by:

$$Operator\ cost = No.of\ shifts * No.of\ operators * Salary/month * 12\ months$$

$$Operator\ cost = 5 * 5 * 30{,}000\ SEK/month * 12\ months = 9\ MSEK$$

A supervisor cost of 15 % on operators' costs (Ulrich & Vasudevan, 2004):

$$Supervisor\ cost = 0.15 * Operator\ cost = 1.35\ MSEK$$

Utility Consumption – Pumps and Compressor
For the pumps and the compressor, the net energy requirement was found in ASPEN. However, the energy requirement for pump 3 is low and will be neglected in the total energy summary.

Utility Consumption – Reactor 1
In reactor 1, the mixing is assumed to happen by sparging with the incoming air. However, the heating coils require energy. This is estimated by investigating the heat transfer from heat exchanger 1 in the ASPEN simulation, which is 28,890 kW. The annual energy requirement is 231,128,000 kWh.

$$Annual\ energy\ requirement_{reactor\ 1} = 28{,}890\ kW * 8000\ h = 231{,}128\ MWh$$

The energy needs for the heating in reactor 1 is very large and would lead to high energy costs. To reduce this cost, the stream will be heat exchanged with other warmer streams in the process. For the heat exchange, an efficiency of the heat transfer is assumed to be 70 %, due to some energy losses.

First, the potential of the outgoing stream from reactor 1 will be evaluated. The specific heat capacity is approximated to be 4175 J/(kg*K) for the outgoing stream, which is the value for 40 °C (Alveteg, 2020). With a mass flow in the outgoing stream of 860,933 kg/h, it gives the energy content of the stream.

$$Energy\ content = 4175\ J/kg * K * 860{,}933\ kg/h = 3594\ MJ/(K * h)$$

The temperature in the flash unit, located in the next step after reactor 1, is 30 °C. This gives a temperature difference of 7 °C (from 37 °C to 30 °C) and this is where it is believed to be room for energy exchange.

$$Energy\ exchange = 3594\ MJ/(K * h) * 7\ K * 70\ \% = 17{,}610\ MJ/h$$

$$\rightarrow \frac{17{,}610\ MJ/h}{3600\ s/h} * 8000\ h/year = 39{,}133\ MWh/year$$

Next to be evaluated is the outgoing stream from the flash. The specific heat capacity is approximated to be 4175 J/(kg*K) for the outgoing stream, which is the value for 30 °C (Alveteg, 2020). With a mass flow in the outgoing stream of 833,497 kg/h, it gives the energy content of the stream.

$$Energy\ content = 4175\ J/kg * K * 833{,}497\ kg/h = 3480\ MJ/(K * h)$$

The temperature in reactor 2, located in the next step after the flash, is 15 °C. This gives a temperature difference of 15 °C (from 30 °C to 15 °C) and this is where it is believed to be room for energy exchange.

$$Energy\ exchange = 3480\ MJ/(K * h) * 15\ K * 70\ \% = 36{,}540\ MJ/h$$

$$\rightarrow \frac{36{,}540\ MJ/h}{3600\ s/h} * 8000\ h/year = 81{,}200\ MWh/year$$

With the suggested heat exchange of the ingoing stream of reactor 1 with the outgoing stream from reactor 1 and the outgoing stream from the flash, the annual energy requirement would be reduced to 110,795,000 kWh.

$$Annual\ energy\ requirement_{reactor\ 1_{reduced}} = 231{,}128\ MWh - 39{,}133\ MWh - 81{,}200\ MWh = 110{,}795\ MWh$$

Utility Consumption – Reactor 2

The rule of thumb for liquid-liquid mixtures is followed to estimate the energy needed for stirring. The power need is 5 hp/1000 gal (Hall, 2012). Translated into suitable units and adapted to the volume in the tank, it gives an annual energy requirement of 480,000 kWh. It is here assumed that the tank volume stated in section 4.1.5, gives an estimated liquid volume of 64 m^3, which is 80 % of the total tank volume.

$$Annual\ energy\ requirement_{stirring} = 60\ kW * 8000\ h = 480{,}000\ kWh$$

The dissolution of sulphuric acid in an aqueous solution is an exothermic reaction, which means heat will be released. The heat of dissolution is -96.2 kJ/mol for sulphuric acid in pure water at 15 °C (Martínez, 2020). To determine if heat exchange is needed, the temperature increase it would cause will be examined. Here it is assumed that the liquid in the tank can will have the characteristics of pure water. The specific heat capacity is approximated to be 4.2 kJ/(kg*K).

$$Heat\ of\ dissolution = -96.2\ kJ/mol * 4243\ mol/h = -408{,}167\ kJ/h$$

The heat of dissolution corresponds to a temperature increase of about 1.5 K/h, which is considered to be negligible. Therefore, the only power consumption in reactor 2 is considered to be that of the stirring.

$$\Delta T = \frac{heat}{c_{p_{H2O}15°C} * m_{H2O}} = \frac{408{,}167\ kJ/h}{4.2\ kJ/(kg * K) * 64{,}000\ kg} = 1.5\ K/h$$

Utility Consumption – Flash

The flash unit is assumed to operate without any energy requirement for the separation, but energy is needed to avoid cooling. In ASPEN it was found that the net duty is -6410 kW. This means 6410 kW needs to be added to avoid the cooling. Furthermore, it gives an annual energy consumption of:

$$Annual\ energy\ requirement_{flash} = 6410\ kW * 8000\ h = 51{,}280{,}000\ kWh$$

Utility Consumption – Filter

The energy consumption cost can be estimated by looking at the energy requirements of a suitable filter unit. The Vacuum drum filter YU with a filter area of 35 m^2 has a power requirement of 45 kW for the drum drive (Andritz Separation, 2020). This results in an annual energy consumption of 5,040,000 kWh for the 14 filter units.

$$Annual\ energy\ requirement_{drum\ drive} = 14 * 45\ kW * 8000\ h = 5{,}040{,}000\ kWh$$

In addition to the drum drive, the energy consumption of both a vacuum pump as well as pumps to assist the permeate flow needs to be added. With the assumption that 98 % wt. of the FDCA is retrieved in the filter cake (Bello, *et al*., 2020), and that the moisture in the filter cake can be neglected, the following size determination was done. The total permeate flow is found to be 803,956 L/h. This flow is based on the assumption that the permeate flow consists of only water, sulphuric acid and the 2 % FDCA that was not retained by the filter. The energy requirement is calculated on the combined stream size out of the 14 filter units. The Vacuum drum filter YU has pumps built-in in the design; hence the power requirement would be divided between the units. The stream data found in Table 9.5 were used for the calculations of the energy requirement.

Table 9.5. Data taken from the simulation in ASPEN Plus; mass flows and volumetric flows for the compounds in the ingoing stream to the filter unit.

ASPEN Plus parameters	m_{H2O}	m_{H2SO4}	m_{FDCA}	F_{H2O}	F_{H2SO4}	$F_{total\ flow}$
(kg/h)	803,378	411	28,346			
(L/h)				803,378	225	831,391

$$m_{FDCA_{retentate}} = 0.98 * m_{FDCA_{in}} = 27{,}779\ kg/h$$

$$m_{FDCA_{permeate}} = m_{FDCA_{in}} - m_{FDCA_{retentate}} = 567\ kg/h$$

$$F_{FDCA_{permeate}} = \frac{m_{FDCA_{permeate}}}{\rho_{FDCA}} = \frac{567\ kg/h}{1.83\ kg/L} = 353\ L/h$$

$$F_{total_{permeate}} = F_{FDCA_{permeate}} + F_{H_2SO_4} + F_{H_2O} = 353\,L/h + 225\,L/h + 803{,}378\,L/h = 803{,}956\,L/h$$

$$W = \frac{m_{total_{permeate}} * v^2}{2} = \frac{m_{total_{permeate}} * J_{membrane}{}^2}{2}$$

$$m_{H_2SO_{4permeate}} = F_{H_2SO_4} * \rho_{H_2SO_4} = 225\,L/h * 1.83\,kg/L = 411\ kg/h$$

$$m_{H_2O_{permeate}} = F_{H_2O} * \rho_{H_2O} = 803{,}378\,L/h * 1\,kg/L = 803{,}378\ kg/h$$

$$m_{total_{permeate}} = m_{FDCA_{permeate}} + m_{H_2SO_{4permeate}} + m_{H_2O_{permeate}}$$

$$m_{total_{permeate}} = 567\ kg/h + 411\ kg/h + 803{,}378\,kg/h = 804{,}356\ kg/h$$

$$W_{vacuum\ pump} = \frac{223\ kg/s * (0.000625\ m/s)^2}{2} = 4.4 * 10^{-5}\ W$$

$$Annual\ energy\ requirement_{vacuum\ pump} = 4.36 * 10^{-5}\ W * 8000h = 0.00035\ kWh$$

The vacuum pump needs $4.4*10^{-5}$ W to operate; this results in an annual energy consumption of 0.00035 kWh. This is a very low energy consumption compared to the rest of the equipment and will be neglected in the total energy requirement calculations.

Another pump is needed to assist the permeate flow. The same principle as the one used to approximate the energy requirement of the vacuum pump, is used. However, the velocity used here is the one that is applicable in the pipes out from reactor 2.

$$Wpump_{permeate\ flow} = \frac{m_{total_{permeate}} * {v_{pipe}}^2}{2}$$

Applying the rule of thumb that the preferred liquid velocity in pipes is somewhere between 1.5-4 m/s (Hall, 2012), a velocity was chosen within the range: 3 m/s. With s volumetric flow rate of 0.22 m^3/s, it gives a cross-sectional pipe area of 0.074 m^2, which equals a pipe diameter of 0.31 m, which is considered reasonable.

$$A_{cross-section_{pipe}} = \frac{F_{perm}}{v_{pipe}} = \frac{0.22\ m^3/s}{3\ m/s} = 0.074\ m^2 \rightarrow d_{pipe} = 0.31\ m$$

By using the chosen velocity, it gives an annual energy requirement of 8044 kWh to transport the permeate flow from the filter unit. This is also a fairly low value and will be neglected in the annual energy consumption.

$$Wpump_{permeate\ flow} = \frac{223\ kg/s * (3\ m/s)^2}{2} = 1005\ W$$

$$Annual\ energy\ requirement_{permeate\ pump} = 1.005\ kW * 8000\ h = 8044\ kWh$$

Water consumption

On an annual basis 6,281,300 m^3 of water is used. The price for water is found to be 23.82 SEK/m^3 (VASYD, 2020). The cost for the water is:

$$Cost\ for\ water = 6{,}281{,}300\ m^3 * 23.82\ SEK/m^3 = 150\ MSEK$$

$$\begin{aligned} Total\ direct\ cost \\ &= 2271\ MSEK + 2221\ MSEK + 150\ MSEK + 112\ MSEK + 1.3\ MSEK \\ &+ 9\ MSEK + 1.4\ MSEK = 4765\ MSEK \end{aligned}$$

Indirect Cost

Cost overhead for staff is estimated to be 70 % on operators cost, resulting in 6.3 MSEK per year.

$$Overhead\ for\ staff = 0.7 * 9\ MSEK = 6.3\ MSEK$$

Cost for administration is assumed to be 25 % on staff overhead, which equals to 1.6 MSEK per year.

$$Administration = 0.25 * Overhead\ for\ staff = 1.58\ MSEK$$

9.8.3 Overall Cost of Production

The cost of FDCA/tonne is:

$$Cost/tonne\ FDCA = \frac{4867\ MSEK}{200{,}000\ tonne} = 24{,}300\ SEK/tonne$$

The cost for enzymes out the total cost is:

$$Cost\ for\ enzymes\ out\ of\ total\ cost = \frac{2204\ MSEK}{4867\ MSEK} * 100\ \% = 45\ \%$$

9.8.4 Sensitivity Analysis

HMF is estimated to be bought for 2271 MSEK/year currently.

$$Cost\ HMF_{-50\ \%} = 0.5 * 2271\ MSEK = 1136\ MSEK$$

$$Cost\ HMF_{+100\ \%} = 2 * 2271\ MSEK = 4542\ MSEK$$

The reagent cost estimated to be 2221 MSEK per year.

$$Cost\ reagents_{-50\ \%} = 0.5 * 2221\ MSEK = 1110\ MSEK$$

$$Cost\ reagents_{+100\ \%} = 2 * 2221\ MSEK = 4441\ MSEK$$

Feedstock and reagent costs are both included in the direct costs, leaving the indirect costs and the capital cost unaffected in this sensitivity analysis. The resulting overall cost of production and cost per tonne produced FDCA, when including both the reduced cost and the doubled cost of the components can be seen in Table 9.6.

Table 9.6. Overall annual cost for the FDCA production, including the results of the sensitivity analysis done on feedstock cost and on reagents' cost.

	Cost (MSEK)		
	Baseline-case	**Both components -50 %**	**Both components +100 %**
Capital cost	239	239	239
Operating cost (direct cost)			
- **Feedstock**	2271	*1136*	*4542*
- **Reagents**	2221	*1110*	*4441*
- **Electricity**	112	112	112
- **Maintenance and repair**	10	10	10
- **Operators**	9	9	9
- **Supervisors**	1	1	1
Operating cost (indirect cost)	8	8	8
Total cost per year (MSEK)	***4870***	***2624***	***9362***
Cost per tonne FDCA (SEK/tonne)	***24,400***	***13,100***	***46,800***