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Techno-economic feasibility analysis of a secondgeneration ethanol plant using the solid part of digestate as feedstock

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MSc. Thesis

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Abstract

Second-generation ethanol is a technology that has been investigated to solve the dilemma of food vs. fuel that the development of biofuels is facing. However, the large scale production of biofuels presents some challenges. The costs to produce it and the process are very dependent on the feedstock. Process modeling can help to verify where the techno-economic bottlenecks of the production process are. This work is an evaluation of the attempt to produce second-generation ethanol from the solid part of the digestate from the anaerobic digestion process of manure. This work presents a detailed process model with the feedstock handling, pretreatment, enzymatic hydrolysis, fermentation, separation, and purification of ethanol, steam and power generation, and wastewater treatment and simulates this process in SuperPro Designer, in two scenarios: grass-root plant and an optimistic version using the facilities available at Twence B.V.

Projected ethanol yields were 123,02 l/dry metric ton biomass using dilute alkali as the pretreatment technology. The feedstock is considered a source of revenue in the optimistic scenario and free of costs for the grass-root scenario, the cellulase cost is $\epsilon 0,18$ per liter of ethanol produced, and sodium hydroxide cost is ϵ 0,59. The plant projected can process 150.000 metric tons of feedstock per year, and the capital cost reached 55.4 M ϵ for the grass-root scenario and 33.7 M ϵ for the optimistic one. The ethanol production cost is ϵ 1,42 and 2,51 per liter in the optimistic scenario and the grass-root scenario, respectively. The water consumption of the plant reaches 24.1l of water per kg of ethanol produced.

The comparison with other projects that used lignocellulosic feedstock to produce ethanol showed that the cost of production is higher when the solid part of the digestate used as feedstock. The reasons for that are the lower content of carbohydrates and the losses of sugars during the pretreatment process. With that, other alternatives may try to mix the solid part of the digestate with another feedstock richer in carbohydrates, to investigate the effects of other pretreatment technologies or to explore the possibility to integrate the anaerobic digestion process with pyrolysis to increase the production of biogas.

Keywords: Solid part of digestate, second-generation ethanol, dilute alkali pretreatment, process model, process economics

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1 Introduction

The human activity is responsible for many changes in the environment, since the industrial revolution. Increase in the life expectancy, health conditions and wealth of the people are examples of these changes, however all this development brought some consequences. In this beginning of the XXI century the humanity is facing a challenge, until now this development is mainly fueled by fossil fuels, which has resulted in an increase in the carbon dioxide levels in the atmosphere, reaching the highest levels in 650.000 years [\[1\]](#page-56-2). This fact is pointed as the reason of the increasing in the average temperature of the Earth, which has already increased around 1°C since 1880. The consequences of the called global warming have been already percepted by the losing mass of the Earth's polar ice sheets and the increase of the sea level [\[2\]](#page-56-3), [\[3\]](#page-56-4).

One of the activities that contributes to increase the content of greenhouse gases in the atmosphere is agriculture. The UN Food and Agriculture Organization estimates that agriculture is responsible for between 14 and 18% of all anthropogenic greenhouse gases emissions, comparable with the estimation for the transportation sector [\[4\]](#page-56-5). While the majority of global warming activities give off carbon dioxide, the agricultural sector primarily emits CH_4 and N₂O. Livestock such as cattle produce methane as part of their digestion cycle. In fact, the CH⁴ produced from enteric fermentation represents almost half of the emissions from the Dutch agricultural sector, and manure management represents 21% [\[5\]](#page-56-6).

1.1 Project background

Thinking about the importance of the manure management and in the possibility to produce a source of energy from its emissions, Twence B.V. a company formed by a conjunction of 16 municipalities located in Hengelo, in the Netherlands, is planning to build an anaerobic digestor near the village of Zenderen with the capacity of process 250,000 tons/year of manure from livestock and with a biogas production of 5 M Nm^3 /year with an investment of ϵ 15-20 M. Between the by-products produced by the anaerobic digestion process, the solid part of the digestate is an organic compost that should be investigated for the production of value-add products, as second generation ethanol.

1.2 Aim and purpose

The aim of this work is to evaluate the techno-economic feasibility of a biorefinery that uses the solid part of the digestate as a feedstock to produce ethanol.

1.3 Thesis outline

This work is divided in seven chapters. In the first chapter an introduction of the topic as well as the aim of this work is presented. In the second chapter a literature review is done taking into account the main concepts used to develop a model for the second-generation ethanol plant and also a review of the works that already used solid part of the digestate to produce second-generation ethanol. In the third chapter the methods and the assumptions to develop the model are presented. The obtained results and a discussion about the results take place in chapter four. Chapter five explores other alternatives for the digestate uses in a circular economy context. Chapter six presents the main conclusions about the project and finally in chapter seven the reccomendations obtained from this work are exposed.

2 Theoretical background

2.1 Second generation ethanol

The necessity to develop alternative fuels to reduce the oil dependency and the pollutants emissions is increasing. However, alternative products from a renewable source usually have a costly production, which makes it hard to promote research, investments, and to achieve the consumer [\[6\]](#page-56-7). Based on this scenario, the second generation ethanol arises, which is a fuel originated from the enzymatic hydrolysis and fermentation of the biomass residues, for instance, sugar cane bagasse, corn stover, or wheat straw. Besides the renewable source, as mentioned before, the process has a high cost.

The scale production of ethanol as fuel started in Brazil, in 1975, with the Federal Government's ProAlcool Program, followed by programs in the USA in 1978. These programs were a response to the oil crises in the 1970s. In 2018, the USA produced 56% of the world production, followed by Brazil with 28% and European Union, 5%. Moreover, ethanol production has been continuously increasing [\[7\]](#page-56-8).

First-generation ethanol is produced through the fermentation of starches and sugars, and it is the most common ethanol available as fuel. A recent debate put under suspect the sustainability of the first generation fuel since they are produced with the same feedstock as food. The worries are that an increase in the first generation fuel production will compromise food production or inflate its price [\[8\]](#page-56-9). The second-generation ethanol is a technological answer for this dilemma. The feedstock used for its production is the lignocellulosic biomass, which does not compete with food production, on the contrary, it can be a by-product [\[9\]](#page-56-10), Figure [1](#page-10-3) presents a scheme of the process design of a second-generation ethanol plant.

Figure 1: Scheme showing the second generation ethanol production process.

The sources of fermentable sugars for the bioethanol are cellulose and hemicellulose; they are the fibers that compound the cell wall of biomass. Cellulose and hemicellulose are biopolymers made, mainly, with monomers of glucose and xylose, respectively. Comparing with the first generation ethanol production process, the second-generation has some extra steps, since the sugars are not readily available for fermentation. The breakdown of these fibers and the molecular separation of the monomers is needed to reach the sugars that can be fermented, and these processes add costs and risks to the production [\[10\]](#page-56-11).

2.2 Lignocellulosic biomass

There are six main groups among the lignocellulosic materials to produce ethanol, softwood and hardwood, cellulose residues (newspaper paper and office paper), herbaceous biomass (grasses), solid municipal residues and agricultural residues (sugar cane bagasse, corn stover, wheat straw, rice straw, manure, digestate, and so on) [\[11\]](#page-56-12).

The lignocellulosic materials are fibers able to build a complex vegetable structure due to the relation among their principal compounds, like cellulose, hemicellulose and lignin [\[12\]](#page-56-13). Figure [2](#page-11-2) presents a scheme of the

main compounds of the lignocellulosic material. The hydrogen bonds that link cellulose molecules determine the rigid structure of them. Lignin evolves the two other components and acts as a physical barrier for microorganisms and water [\[13\]](#page-56-14). Hemicellulose links cellulose and lignin forming the fiber. However, because of this complex structure, the conversion of biomass in bio-based products is hampered [\[11\]](#page-56-12).

Figure 2: Structure of lignocellulosic material, adapted from [\[14\]](#page-56-1). Lignin is composed, mainly, of three major components, H (p-coumaryl alcohol), G (coniferyl alcohol) and S (sinapyl alcohol).

2.2.1 Cellulose

Cellulose, $(C_6H_{10}O_5)_n$, is the most abundant organic compound on Earth and is the major structural component of the cell wall of higher plants [\[15\]](#page-56-15). Cellulose is commonly used for paperboard and paper production, but also converted to cellophane and rayon and, more recently, to cellulosic ethanol [\[16\]](#page-56-16).

Cellulose is formed by glucose units linked by $\beta(1-4)$ bounds. The structural function of cellulose is possible due to its insolubility in water under normal conditions [\[17\]](#page-56-17). Its structure can be classified into two types, crystalline and amorphous. The amorphous material does not present a defined form, and the regions where a sequence is respected are known as crystalline [\[13\]](#page-56-14).

Some ruminant animals can digest cellulose with the help of symbiotic anaerobic bacteria that are located in the flora of the rumen, and these bacteria produce enzymes that can breakdown the cellulose structure [\[18\]](#page-56-18). Celluloses that have a high content of amorphous cellulose are usually more easily digested by the enzymes [\[19\]](#page-56-19). After the digestion of cellulose, the animals can obtain sugars and transform these sugars into energy, similar to the process done to produce ethanol.

2.2.2 Hemicellulose

Hemicellulose is a heteropolymer present with cellulose in almost all plant cell walls. Hemicelluloses contain different sugar monomers, besides glucose: five-carbon sugars, xylose and arabinose, the six-carbon sugars, mannose and galactose, and the six-carbon deoxy sugar rhamnose are also present. However, the presence of xylose is predominant [\[20\]](#page-58-0).

Comparing with cellulose, they present a more random and amorphous structure, a low degree of polymerization and are less resistant to chemicals, especially acids, and they are soluble in alkali solutions. The presence of hemicellulose with cellulose contributes to the flexibility of the fibers [\[21\]](#page-58-1).

Studies have been focused to convert both cellulose and hemicellulose to ethanol [\[22\]](#page-58-2). Even though glucose fermentation is an established technique, conversion of xylose is a limiting factor. For that, genetic engineering is trying to create yeasts that can be able to ferment xylose [\[23\]](#page-58-3).

2.2.3 Lignin

Lignin is the second most abundant biopolymer after cellulose. Despite its availability, lignin is mostly combusted for process steam and electricity generation, as a by-product from the pulp and paper industry [\[24\]](#page-58-4). The aromatic building blocks of lignin, so-called monolignols, make it an attractive feedstock for direct synthesis of specialty and fine aromatic chemicals. However, only a marginal part of the lignin produced worldwide is valorized into other products, such as dispersant in cement and gypsum, emulsifier and a chelating agent in the treatment of industrial effluents [\[25\]](#page-58-5).

Lignin is a substance that gives rigidity to the cell wall. It is formed basically by fenilpropane units that form a tridimensional and amorphous molecule and a non-homogeneous structure. The monomers that form lignin are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [\[13\]](#page-56-14).

2.2.4 Other substances

There are other substances present in the lignocellulosic biomass. Pectins are a complex family of polysaccharides that are part of the cell wall and easily extracted [\[26\]](#page-58-6). Extractives are solubles components that include resins and terpenoids [\[27\]](#page-58-7). Also, the ashes and inorganic residues, that leave after the total combustion in high-temperature [\[28\]](#page-58-8).

2.3 Anaerobic digestion (AD)

In this projet it will be evaluated the potential of the solid part of the cattle manure digestate as a feedstock for the production of ethanol. The anaerobic digestion is a process where microorganisms digest biodegradable material in the absence of oxygen. This process is used at industrial and domestic scale to produce food, drinks, fuels, and to manage wastes. In this work, the anaerobic digestion that interest is the one that happens in the biodigesters that degrade manure from farms to produce biogas and the liquid and solid part of the digestate, Figure [3](#page-12-3) shows a scheme of the anaerobic digestion process.

Figure 3: Scheme of the anaerobic digesttion process.

Anaerobic bacteria are the microorganisms responsible for the decomposition in biodigesters by attacking the structure of the organic materials, breaking them into simple compounds like methane and carbon dioxide [\[29\]](#page-58-9).

The decomposition of matter depends on the interaction of three groups of bacteria: fermentative or acidogenic substances that hydrolyze complex compounds into simple ones; acetogenic, which produce acetate and hydrogen; and methanogenic, which produce methane and carbon dioxide [\[30\]](#page-58-10).

The digestion process can be broken in four steps: 1)Hydrolysis, where the polymers, which are compounds of the most complexes such as starch and protein are transformed into monomers, which have simpler chains like sugars and amino acids; 2) Acidogenesis, where monomers are transformed into volatile fatty acids; 3) Acetogenesis, where the volatile fatty acids are converted to acetic acid, gas carbonic and hydrogen and finally, 4) Methanogenesis, where acetic acid is transformed into methane and carbon dioxide [\[31\]](#page-58-11).

The indigestible material and dead microorganisms are the digestate, that is composed by a liquid and a solid part. These parts can be mechanically separated by screw press, decanters, belt filter presses, screens, and flotation. The liquid part is rich in nitrogen and can be used immediately to grow crops [\[32\]](#page-58-12).

2.3.1 Solid part of the digestate - SPD

The solid part of the digestate is a by-product from the anaerobic digestion process. The major components of the solid digestate are cellulose and lignin. Due to the two digestions, the most accessible carbohydrates are already digested. For this reason, this material is known as "recalcitrant" and presents low nutrient value [\[33\]](#page-58-13). Its use has been limited to soil amendment or animal bedding [\[34\]](#page-58-14). However, some studies [\[35\]](#page-58-15), [\[36\]](#page-58-16), [\[37\]](#page-59-1), and [\[38\]](#page-59-0) have demonstrated the suitability of the solid digestate as a lignocellulosic feedstock for the production of fuels or value-added products.

In this work it is assumed that SPD comes from an anaerobic digestor that receives as feedstock only dairy cattle manure. Other types of digestate, for instance, digestate from pig manure and digestate from poultry manure, are not considered because their fiber content is lower than in cattle manure [\[39\]](#page-59-2). SPD from cattle manure is composed, in general, by 10-35 wt.% cellulose, 20-30 wt.% hemicellulose, $2-25\%$ lignin, and 8-35%ashes [\[40\]](#page-59-3). The solid part of the digestate can vary in composition and moisture content due to animal food, animal species, region, weather, storage, anaerobic digestion practices, and so on [\[40\]](#page-59-3)

Inorganics are also present in the composition of SPD. Unfortunately, information of the main minerals in the solid part of the digestate is scarce. Then, to evaluate the effects of the elements in the ethanol production process the content of the elements in the fresh dairy manure was considered. In general, the main inorganic components in fresh manure are calcium, potassium, phosphorus, magnesium and sodium [\[39\]](#page-59-2), [\[41\]](#page-59-4), [\[42\]](#page-59-5).

Chen et al., 2003 [\[39\]](#page-59-2) investigated the possibility of production of ethanol from fresh manure. During the experiments, they verified that nitrogen and calcium are harmful to the conversion process for different reasons. The nitrogen content of fresh manure is linked with the protein content, and when protein in the presence of sugar is heated above 140°C, these components react and form other products that make sugars unavailable for fermentation. This phenomenon is a type of non-enzymatic browning reaction known as Maillard reaction, and it is a group of chemical reactions widespread in food industries to produce aroma and high molecular weight brown polymers [\[43\]](#page-59-6).

Also, they tested the performance of the enzymes with the elements presented in fresh manure, and they verified that the presence of calcium in the feedstock has harmful effects on the performance of the enzymes. Elliot et al., 2004 [\[44\]](#page-59-7), and by Min et al., 2017 [\[45\]](#page-59-8) also mentioned this, when calcium is in the form of calcium carbonate. The pointed reasons for that are the increase in the pH of the solution formed during the process $[45]$, non-productive enzyme binding due to the high affinity of $CaCO₃$ to cellulase, and blocking access to the cellulosic fibers. Kuno et al. (1961) [\[46\]](#page-59-9) observed that the ion Ca^{2+} causes the deactivation of the enzymes due to aggregation, preventing some fiber places to be reached.

The anaerobic digestion process does not influence the total nitrogen content on the digestate [\[32\]](#page-58-12). To prevent sugar losses due to Maillard reactions it is advisable to keep the ethanol conversion process under mild temperature conditions [\[47\]](#page-59-10). For calcium, the anaerobic digestion process reduces the presence of it; however, it persists [\[36\]](#page-58-16), [\[38\]](#page-59-0). To prevent the presence of calcium carbonate in the fibers during the enzymatic hydrolysis process of waste office paper, Wang et al, 2011 [\[48\]](#page-59-11), washed the fibers with an acid solution, and Goss et al., 2007 [\[49\]](#page-59-12) reached solubility of calcium carbonate of $46mg/ml$ in an environment of pH 4.5.

Another consequence of the anaerobic digestion process is the reduction of the particle size of the fibers. During the experiments Yue et al., 2011 [\[37\]](#page-59-1) verified that after the anaerobic digestion the particles smaller than 0.3 mm increased from $15wt \%$ to around $38wt \%$ of the total dry matter.

2.4 Production of second-generation ethanol from SPD

A scheme of the process to produce second-generation ethanol has been already showed in Figure [1,](#page-10-3) from now on the sections of this process will be explained to have an overview of the second-generation ethanol production process.

2.4.1 Pretreatment

Pretreatment is the process where chemicals and energy are used to make the fibers more reactive to the enzymatic hydrolysis process and to convert fibers into sugars. Desirable features of a pretreatment process in second-generation ethanol plant include the avoidance of biomass size reduction, preservation of hemicellulose, limiting the fermentation inhibitors formation, minimization of the energy consumption and being cost-effective, and so on [\[50\]](#page-59-13).

Different pretreatments are commercially available, or under research, they are usually classified according to the method used to process the fibers. Physical pretreatment methods are considered more environmentally friendly and are relatively simple; however, they are energy-intensive, therefore costly. Mechanical pretreatment and steam explosion are the most common of the physical pretreatments [\[51\]](#page-59-14), [\[50\]](#page-59-13).

Chemical pretreatment methods use chemical substances to open the lignocellulosic structure, it is a prevalent method in pulp and paper industry, and the most common chemical pretreatments are acid and alkali pretreatments, for both a dilute version use fewer chemicals, the other types of pretreatment are organosolv, ionic solvents and oxidation. Physicochemical pretreatments are processes that use physic and chemical principles to open the lignocellulosic structure, the most common is steam explosion, but other examples are ammonia fiber expansion, carbon dioxide explosion and sulfur dioxide explosion and electrical catalysis. Finally, biological pretreatments use some microorganisms to degrade lignin, but they are time-consuming [\[52\]](#page-60-0).

The selection of the pretreatment for application in a second-generation ethanol plant takes into account several criteria, for instance, cellulose yield, hemicellulose yield, glucose concentration after hydrolysis, the designed temperature and pressure, the pretreatment time, fermentation compatibility, pretreatment capital cost, chemical costs, water use, toxicity and waste disposal [\[53\]](#page-60-1). Overall these criteria it should be take into account the feedstock used, for the solid part of the digestate the most reported pretreatments used are dilute acid and dilute alkali [\[35\]](#page-58-15), [\[36\]](#page-58-16), [\[37\]](#page-59-1), [\[38\]](#page-59-0). Then, based on the criteria mentioned, these two pretreatments will be evaluated in the following paragraphs.

2.4.1.1 Dilute alkali Dilute alkali is one type of chemical pretreatment of lignocellulosic material that promotes an increase in the digestibility of this material to produce biofuels and biochemicals. The alkaline pretreatment of biomass is an old process in the pulp and paper and the textile industries, also known as mercerization [\[54\]](#page-60-2).

Sodium hydroxide (NaOH) is the most common chemical utilized for this pretreatment. It is considered adequate to increase the availability of sugars for hardwood and agricultural residues that have low lignin content. Others chemicals such as calcium hydroxide [\[55\]](#page-60-3), potassium hydroxide [\[56\]](#page-60-4), hydrazine, and anhydrous ammonia are also used in dilute alkali pretreatments.

During the reaction of the lignocellulosic material, the dilute alkali solution causes swelling of the lignocellulosic material, altering the structure of biomass, increasing the internal surface area and decreasing the degree of polymerization and the cellulose crystallinity [\[57\]](#page-60-5). Swelling is caused by solvation and saponification of biomass. Saponification occurs on the intermolecular ester bonds cross-linking xylan hemicelluloses and other components, resulting in the porosity increasing and the cleavages of the cross-links. The increasing swelling capacity of biomass can be due to lignin removal [\[58\]](#page-60-6).

2.4.1.2 Dilute acid The acid-based pretreatments of the lignocellulosic structure can be supplemented with mineral acids or acetic acid is formed due to hydrolysis of hemicellulose acetyl linkages and degradation of polysaccharides/lignin to short-chain aliphatic acids and phenolic acids [\[27\]](#page-58-7). Acids provoke the hydrolytic

cleavage and removal of hemicellulose and lignin, hence improving the accessibility of residual cellulose to enzymes [\[59\]](#page-60-7).

Initially, the acidic processes were applied to biomass to obtain furfural from hydrolysis of hemicellulose [\[60\]](#page-60-8). Dilute acid treatment generally refers to the hydrolysis of cellulose and hemicellulose to a monosaccharide with acid concentration below 10wt.% as catalyst [\[51\]](#page-59-14).

2.4.1.3 Comparison of dilute alkali and dilute acid pretreatments The cellulose and hemicellulose yields after pretreatment were evaluated based on the data available in some studies, and presented in Table [1.](#page-15-0) With the available data, it is possible to see that the sum of the carbohydrates yield is higher for the dilute alkali process since the acid process do not recover any hemicellulose. Another reason for the higher recovery in the dilute alkali process is that the solid part of the digestate is already alkali, so the effect of one alkali environment is boosted with this feedstock [\[36\]](#page-58-16).

Source		[37]	[37]	[35]	[35]	[38]	[36]	[37]	[37]	$\left[35\right]$
AD Reactor		CSTR.	PFR.			\equiv	$\overline{}$	CSTR	PFR.	CSTR
Pretreatment		NaOH	NaOH	NaOH	NaOH	NaOH (15psi)	NaOH	H_2SO_4	H ₂ SO ₄	H ₂ SO ₄
Concentration	$\mathrm{wt.}\%$	$\overline{2}$	$\overline{2}$		$\overline{2}$	0.08	3	3	3	
Time	h	3	$\overline{2}$	$\overline{2}$	$\overline{2}$		3	$\overline{2}$	$\overline{2}$	$\overline{2}$
Temperature	$^{\circ}C$	130	130	130	130	121	130	130	130	130
Moisture	$\text{wt.}\%$	٠				85.7	$\overline{}$			
Dry matter	$\mathrm{wt.}\%$	٠				14.3	6			
Fiber	$\%dm$	84.3	76	$81.5 + 2.1$	$75.9 + 1.1$	70.1 ± 0.1	83.4	86.9	89.3	83.3 ± 3.0
Cellulose	%dm	61.6	48.2	49.3 ± 0.5	48.2 ± 0.4	31.8 ± 0.0	45.3 ± 2.4	45.7	43.8	43.2 ± 0.7
Hemicellulose	%dm	8.3	4	8.7 ± 0.6	3.9 ± 0.5	18.2 ± 0.0	17.6 ± 1.3	Ω	Ω	0
Lignin	$\%$ dm	14.3	23.8	23.5 ± 1.0	23.8 ± 0.2	20.1 ± 0.1	20.5 ± 0.7	41.3	45.6	40.1 ± 2.3

Table 1: Literature review - yields of cellulose and hemicellulose after pretreatment of SPD.

The glucose concentration after enzymatic hydrolysis can indicate how effective was the pretreatment, in Table [2](#page-15-1) it is possible to verify that for the dilute alkali process the average of the concentration reached $30g/l$, and for the dilute acid is $5g/l$, which reveals that the enzymes can reach the cellulose easily with the pulp treated with dilute alkali than with dilute acid.

Table 2: Literature review - yields of glucose after enzymatic hydrolysis of the pretreated SPD.

Source		[35]	[35]	[35]	[36]	[35]
AD Reactor		CSTR	CSTR	CSTR		CSTR
Pretreatment		NaOH	NaOH	NaOH	NaOH	H2SO4
Concentration	$wt.\%$		2	2	3	
Time	h	2	$\overline{2}$	2	3	$\overline{2}$
Temperature	$^{\circ}C$	130	130	130	130	130
Solid loading	$\%(\mathrm{w}/\mathrm{w})$	5	5	10	10	5
Enzyme		Cellulase	Cellulase	Cellulase	Cellulase	Cellulase
Enzyme loading	FPU/gdm	26	26	26	26	26
Glucose conversion rate	$\%$	73	90	95	68.2 ± 5.2	22
Glucose concentration	g/1	20	23	50	29.7 ± 1.3	5

The temperature and pressure conditions for these treatments are somehow similar. Alkaline pretreatment is carried out at low temperature and pressure, and it may be completed at ambient conditions [\[57\]](#page-60-5), and that is one of the main advantages of this process [\[22\]](#page-58-2). The dilute acid pretreatment can be performed at a temperature in the range of 180°C during a short period of time, or at a lower temperature, about 120 °for longer retention time (30-90 min), [\[61\]](#page-60-9). On the other hand, in general, the dilute alkali process might take hours or days to complete the reaction [\[57\]](#page-60-5), specifically for the solid part of the digestate it might take hours to complete the pretreatment [\[35\]](#page-58-15), [\[36\]](#page-58-16) [\[37\]](#page-59-1), [\[38\]](#page-59-0).

When talking about fermentation compatibility, the dilute alkali process better preserves the carbohydrates than the acidic conditions [\[62\]](#page-60-10). Besides, both pretreatments generate inhibitors for the fermentation process. A washing step of the fibers after the dilute alkali pretreatment showed an improvement in the fermentation of sugars in work done by Jonsson et al., 2013 [\[63\]](#page-60-11). The dilute acid process presents a high generation of inhibitory products, such as furfurals, 5-hydroxymethylfurfural, phenolic acids, and aldehydes [\[64\]](#page-60-12), and thus a detoxification process is needed after the pretreatment and overliming is the most used process [\[65\]](#page-60-13).

Qualitatively, the capital cost needed for a dilute alkali process is lower than for acidic conditions [\[66\]](#page-60-14). The cost for the dilute acid pretreatment reactor is high due to the requirement of corrosion-resistant material [\[67\]](#page-61-2). Comparing the two processes for the chemical costs, the cost of sodium hydroxide, the usual base used for the alkali process, is considered a limitation [\[68\]](#page-61-3). Chen et al., 2013 [\[62\]](#page-60-10) considered that an alkali-based biorefinery is less economically attractive unless the cost of chemical recovery can be significantly reduced. For the acidic pretreatment, the cost of sulfuric acid is considered very low when compared with alkaline chemicals.

High water consumption is a fact for both processes, however, for the dilute alkali process, a large quantity of water is needed to remove the salts from the biomass, because it is a hard task process to remove them [\[64\]](#page-60-12). Because of it, the dilute alkali process generates residues that should be treated before going to the environment. The neutralization process of the dilute acid process generates a gypsum waste disposal problem [\[69\]](#page-61-4). Finally, both processes use toxic chemicals, that are very corrosive and can cause severe burns.

Based on the work done by B. Dale and R. Ong, 2012 [\[70\]](#page-61-0), it was possible to build a matrix to compare both pretreatments, as it can be seen in Figure [3.](#page-16-1) Taking into account the matrix, dilute alkali pretreatment is chose as the best option to process the solid part of the digestate, the main reasons for that are the higher levels of recovery of carbohydrates, the alkali characteristic of the feedstock and the higher yields of glucose after the enzymatic hydrolysis process.

Table 3: Matrix to evaluate dilute alkali and dilute acid pretreatments to process the solid part of the digestate. The colors green, yellow and red mean good, regular and bad characteristics of the process, respectively. Based on [\[70\]](#page-61-0).

2.4.2 Enzymatic hydrolysis

The most common methods to hydrolyze biomass are acid hydrolysis and enzymatic hydrolysis. In this work it is more emphasis given to the enzymatic hydrolysis process. Enzymatic hydrolysis is the process that uses

enzymes to break down the lignocellulose structure into simple sugars. It can be operated in mild conditions, and it is a non-intensive energy process, while few fermentation inhibitors products are generated [\[71\]](#page-61-5). For complete cellulose degradation, the synergistic action of three cellulase enzymes is necessary: endoglucanases, exoglucanases, and glucosidase, some systems also include exoglucanglucohydrolase and exocellobiosidase. Endoglucanases significantly reduce the degree of polymerization of the substrate by randomly attacking the interior parts, mainly in the amorphous regions of cellulose. Exoglucanases shorten the glucan molecules by binding to the glucan ends and releasing mainly cellobiose units. Finally, beta-glucosidases split the disaccharide cellobiose into two units of glucose [\[72\]](#page-61-6).

Various forms of these enzymes are present in different species of microorganisms to digest diverse types of celluloses present in nature. Cellulases activity is expressed in terms of the substrates used to quantify them. For instance, filter paper hydrolysis is measured as filter paper cellulase units. For the hemicellulose hydrolysis it is needed to add to the system xylanase and xylosidases. Besides to break down xylan to primarily pentose sugars, xylanases improve the accessibility of cellulases to hydrolyze cellulose fibers [\[71\]](#page-61-5). The desirable characteristics of cellulases for the application in the hydrolysis of cellulose are: 1) high specific activity, which require lower quantities to achieve the same degree of hydrolysis catalytic efficiency; 2) high catalytic efficiency against crystalline cellulose, this will reduce the time required to hydrolyze the crystalline cellulose; 3) high thermostability that can be used at higher temperatures to accelerate the rates of cellulose hydrolysis; 4) resistance to end-product inhibition, with that more concentrated mixtures of sugars can be produced, thus more bioproducts; 5) stability against shear forces, shear-resistant cellulases will be useful where agitation must be provided to suspend the solid cellulose in a hydrolysis reactor [\[71\]](#page-61-5).

Enzymatic hydrolysis is commonly applied to the production of ethanol because the yields of glucose can be easily fermented to ethanol. Some process can be designed to integrate enzymatic hydrolysis and fermentation; for this project, the process strategy studied is to keep both processes separated, in order to have the optimal approach for hydrolysis and fermentation. This process is called separate saccharification and fermentation (SHF), wehre saccharification is a term from biochemistry to designate the hydrolysis of soluble polysaccharides to form simple sugars.

In the separate saccharification and fermentation, cellulose is hydrolyzed first by cellulases in one reactor, followed by fermentation by the yeasts in a second reactor. The main disadvantage of this process is that the high accumulation of sugars inhibites the enzyme activity, affecting the ethanol yields.

A trade-off in this process occurs because to obtain ethanol yields in a way that the distillation costs will not be prohibitive, the ethanol concentration in culture broth needs to be 5% or more, and the cellulose slurry in the hydrolysis process needs to be 10% or more. However, what happens with a high concentration of cellulose in the slurry is that it avoids the mixing process between cellulose and cellulases, resulting in a low conversion yield. This is an issue of the SHF process because long residence time will result in high operating and capital costs per unit of glucose obtained. Then, it requires optimization of several process parameters, such as cellulose concentration, enzyme loading, beta-glucosidase-to-cellulase ratio, reactor conditions (the type of impeller and mixing speed), besides an arrangement of suitable membranes to avoid inhibition of cellulases by the resulting sugars [\[73\]](#page-61-7).

2.4.3 Fermentation

Ethanol fermentation is an old process used in the biotechnology industry, where sugars are converted to cellular energy-producing ethanol and carbon dioxide as by-products. Usually, this process occurs in the absence of oxygen; that is why this process is considered an anaerobic process. However, some yeasts tolerate quite well the presence of oxygen to produce ethanol [\[74\]](#page-61-8).

Currently, industrial ethanol fermentation is done by the yeast Saccharomyces cerevisiae, because of its low pH and high ethanol tolerance and by the bacteria Zymomonas mobilis, because of the high specific ethanol productivity and yield of glucose and sucrose [\[75\]](#page-61-9). Nowadays, most of the studies have been the focus on the creation of xylose-fermenting mutant strains, because none of the mentioned species can ferment xylose [\[76\]](#page-61-10). Another technology that has been testing is to use lignocellulose materials to replace pure glucose for preparation of the fermentation seeds because this can reduce the cost of ethanol fermentation [\[77\]](#page-61-11). A standard measure for the seed inoculation ratio was approximately 10% (v/v) of the fermentation volume [\[78\]](#page-61-1).

The characteristics required by the organisms is that it should give a high ethanol yield and be able to withstand high ethanol concentrations in order to keep distillation costs low [\[79\]](#page-61-12). In addition to these general requirements, inhibitor tolerance, temperature tolerance, and the ability to utilize multiple sugars are essential for SSF application; also tolerance towards low pH-values will minimize the risk of contamination [\[72\]](#page-61-6).

2.4.4 Separation and purification

The separation and purification process is needed to obtain ethanol with a standard quality to sell. In this project, the target is a purity of ethanol of 99.5 wt.%, usually, by-products are mostly removed by distillation. The fermentation broth usually contains around 4 -5 wt.% of ethanol [\[80\]](#page-61-13). Distillation uses the differences in volatilities of the components of the mixture to separate it; low boiling point components are concentrated in the vapor phase, after condensing this vapor, the liquid phase stays more concentrated in the less volatile component. It is an energy-intensive process, but it is the most dominant technique in ethanol production [\[81\]](#page-61-14).

As the water/ethanol mixture has reached the azeotrope concentration at 95.5 wt.% ethanol, further separation to achieve anhydrous ethanol has to be carried out. The final dehydration step determines the quality and cost of ethanol produced. Anhydrous ethanol (>99.5 moles $\%)$ is required to be used as fuel-grade ethanol. One of the techniques to concentrate anhydrous ethanol is a molecular sieve. A molecular sieve is a material with tiny pores of uniform size. The pore diameters are similar in size to small molecules, and thus large molecules cannot enter or be adsorbed. This is what happens with the azeotrope mixture water-ethanol, the molecules of water are absorbed by the molecular sieve and the molecules of ethanol not, then the separation can be done above the azeotrope point [\[82\]](#page-61-15).

2.4.5 Power cogeneration

According to Bejan et al. 2016, [\[83\]](#page-61-16), cogeneration is the simultaneous mechanical and thermal energy production from one or more primary sources of fuel. With biomass as feedstock, it is possible to have a cogeneration plant where the parts of the biomass that cannot be used for ethanol production can be burned in a steam generator and heat steam to generate electricity and heat in a Rankine cycle.

Because lignin has a high heating value and it is not used to produce ethanol, the streams that leave the primary process are rich in lignin, and after an evaporation process, this lignin can fuel the steam and electricity production. This steam and electricity can be directed to the consumption of the process, creating a self-sustained cycle, and the excedent heat and power can be sold to other consumers [\[84\]](#page-62-1).

3 Methods

This section presents the premisses used to design the second-generation ethanol plant. Two projects were planned: the first one is a grass-root project where all the facilities needed for the installation of the project are built from scratch, and the second scenario uses some facilities that Twence B.V. already has in its industrial yard to provide steam and electricity to the ethanol plant.

3.1 Design basis and conventions

3.1.1 Feedstock composition

The feedstock selected for ethanol production is a crucial parameter in the conversion of biomass to ethanol. According to Adriaansn et al., 2019 [\[40\]](#page-59-3) the best feedstock option for a biorefinery in the East Netherlands is the solid part of the digestate from dairy cattle manure anaerobic digestor process. The main reasons for that are the abundant availability and the possibility of revenue from its collection.

Besides the SPD composition can vary due to many factors [\[40\]](#page-59-3), for this analysis it is assumed a constant composition based on Elumalai et al., 2014 [\[38\]](#page-59-0) as Tables [4](#page-20-3) and [5.](#page-20-4)

	Component Solid part of the digestate, wt.%
Cellulose	23.6
Hemicellulose	17.5
Lignin	29.4
Uronic acid	2.6
Ash	13.7
Extractives	11.7
Others	1.5

Table 4: Composition of the solid part of the digestate, adapted from [\[38\]](#page-59-0)

Table 5: Elemental composition of the solid part of the digestate, adapted from Elumalai et al., 2014 [\[38\]](#page-59-0)

Component	Solid part of the digestate, wt. $%$
\overline{C}	39.1
N	3.3
P	1.1
K	1.4
Ca	4.8
Mg	0.8
S	1.0
Cl	0.4
Fe	0.3
Zn	0.1

The designed components for ethanol production are cellulose and hemicellulose. To model these substances in SuperPro some assumptions about the chemical composition of the components of SPD were done. Lignin has a general composition of $C_{19}H_{20}O_6$ and uronic acid $C_5H_8O_6$. Ash is inert throughout the process, and others are modeled as extractives with an average composition $C_6H_{12}O_6$

3.2 Premisses of the process design

A process design is an essential step to make a technical and economic evaluation of a process. With the process design, it is possible to solve mass and energy balances, followed by equipment sizing, investment cost, and variable costs estimations.

This techno-economic analysis is based on simulation results of thermochemical and biochemical processes. The software that this process is designed is SuperPro Designer. With the help of this tool, mass and energy balances were done, as well as equipment sizing. Estimations of the f.o.b (free-on-board) equipment costs are done with correlations from literature, [\[85\]](#page-62-2).

3.2.1 Plant project considerations

The project is designed to process 45.000 t/year (5.67 t/h) of dry SPD, counting in wet basis the annual feedstock requirement is 150.000 t, with an expected 7920 operating hours per year (90% uptime). The process is designed to operate in a continuous form; however, some pieces of equipment are modeled in a batch mode with staggered units to keep the continuous process. This project is planned to be built in the East Netherlands near the actual location of Twence B.V. The feedstock is delivered by a partner company, and the supplier farms are in a radius of 50 km from the biorefinery.

3.2.2 Units

Most of the units present in this work are in the SI units; however, to estimate free on board (f.o.b) costs, some units of the English System are used.

3.2.3 Solid loading

In this process, a conversion of a solid feedstock into a liquid product takes place. Total solid loading is defined as the total weight percent of soluble and insoluble solids in a given material stream. In the starting of the pretreatment and the enzymatic hydrolysis processes the solid loading is kept in 20 wt.% to promote the reduction of viscosity and increase the mass transfer during the process [\[58\]](#page-60-6).

3.2.4 Losses

During all processes, it is assumed that there are no material losses. And, it is also considered that the energy from the reactions, pumping, and agitation of tanks is lost to the environment.

3.3 Overview of the process

An overview of the process can be seen in the Figure [4.](#page-22-0) The process is divided in seven areas: Area 100 - Front-end operations, Area 200 - Pretreatment, Area 300 - Enzymatic hydrolysis, Area 400 - Fermentation, Area 500 - Separation and purification, Area 600 - Boiler, turbine-generator and Area 700 - Wastewater treatment. These areas are described in the following subsections.

3.3.1 Area 100: Front-end operations

The front-end operations handles the incoming feedstock. Figure [5](#page-23-1) shows a scheme with the unit operations designed for this section. In this design, partner companies bring the feedstock from farmers by trucks. The feedstock is homogeneous, and the dry mass content is 30%. The daily requirement of the plant is 454,45 t, including moisture. According to Twence each truck carries 30 ton and that the receiving operates 23 hours a day, five days a week. As the plant operates 7 days in a week, the plant needs to receive about 27.7 t/h, which means more or less one truck per hour. Then, one receiving unit was designed, and it allows an unloaded process of about one hour, more than enough.

The feedstock is driven to storage by a system of solid transport represented by a truck dumper (BC-101). The SPD storage (SL-101) is dimensioned to store materials for five days of production, to prevent some transport or seasonal problems. The feedstock is stored in a building with a flat concrete area (SL-101) [\[86\]](#page-62-3). Because of the two previous digestions of the feedstock, no size reduction was designed for this process [\[37\]](#page-59-1).

Figure 5: Scheme of the designed Area 100 - Front-end operations.

A transfer conveying (BC-102) drives the store feedstock to the solid loading adjustment tank (V-101), where water is added and mixed to the feedstock by agitators, and the solid loading is adjusted to 20wt.%. The water stream to promote the dilution of the feedstock comes from the water storage (V-102), and it is pumped by the solid loading adjustment pump (PM-102). After the solid loading adjustment, the stream is pressurized to 5 bar to avoid evaporation in the pretreatment reactor and pumped to the pretreatment section by the feedstock pump (PM-101).

3.3.2 Area 200: Pretreatment

The main tasks of the pretreatment are to guarantee access to the fibers by the enzymes and to avoid the production of enzyme and yeast inhibitors. The dilute alkali, was selected, as mention in section 2.4.1.3, and it happens in mild conditions to avoid the reactions between nitrogen and sugars [\[87\]](#page-62-4), [\[88\]](#page-62-5). Figure [6](#page-24-0) shows the designed pretreatment process.

Figure 6: Scheme of the designed Area 200 - Pretreatment.

After that, a solid-liquid separation takes place followed by an acidic washing step. These two steps are needed to partially wash out the sodium hydroxide and products from the degradation of sugars, and to solubilize the calcium carbonate. These components can reduce the microorganisms activity in the following processes [\[63\]](#page-60-11), [\[44\]](#page-59-7), [\[45\]](#page-59-8). Calcium carbonate is not one of the components simulated, however, from Chen et al., 2003 [\[39\]](#page-59-2) and Wang et al., 2011[\[48\]](#page-59-11) it is known that calcium íons can reduce the enzymatic activity. The resulting flow is ready to be hydrolyzed in Area 300 - Enzymatic hydrolysis.

The first stage of the pretreatment is a mixing between the diluted feedstock stream (S-106) and the concentrated sodium hydroxide solution (S-210). Then, a heat exchanger (HX-201) acts as a heat recovery system, where the heated stream (S-204) that leaves the reactor heats the stream that is arriving (S-201). This heat is not enough to reach the designed temperature of 130°C, for that, another heat exchanger was designed (HX-202), which receives steam at 152°C to heat the mainstream to the desired temperature.

The pretreatment reactor (R-201) is a continuous reactor projected to resist the conditions of a pressurized stream at 5 bar. The hydrolysis reactions are catalyzed using sodium hydroxide, the parameters of this process are based on the work done by Teater et al., 2011 [\[36\]](#page-58-16) and are summarized in Table [6.](#page-24-1)

Table 6: Pretreatment reactor conditions.

Sodium hydroxide loading	$2wt.\%$
Residence time	3 h
Temperature	$130~^{0}$ C
Pressure	5 _{bar}
Total solids loading	$20 \text{ wt. } \%$

Table [7](#page-25-2) presents the pretreatment hydrolysis reactions and the assumed conversions reactions that occur in the pretreatment reactor. The reactions and the conversions are based on the work done by Kumar et al., 2011 [\[89\]](#page-62-0) and Teater et al., 2011 [\[36\]](#page-58-16).

Reaction	Reactant	% Converted to product
$(Cellulose)_n+nH_2O\rightarrow nGlucose$	Cellulose	38\%
$(Hemicellulose)n+nH2O->nXylose$	Hemicellulose	49\%
$(Lignin)_n$ ->nSoluble lignin	Lignin	62.5\%
$nXylose \rightarrow nFurfural +3nH2O$	Xylose	0.01%
$nGlucose -\geq nHMF + 3nH_2O$	Glucose	0.01%

Table 7: Pretreatment hydrolysis reactions and assumed conversions

After cooling by exchange heat with the incoming stream, the stream (S-205) is directed to a rotary vacuum filtration (RVF-201) where the pulp separation occurs. The filtrate goes to the evaporator, boiler, and turbine section where it will be evaporated and burned, and the cake follows to washing step (WSH-201). During the solid-liquid separation, all the soluble components are directed to the Area 600 - Boiler turbine-generator, including the converted sugars. As stated by Table [7,](#page-25-2) because of the losses and taking in consideration the initial content of cellulose and hemicellulose in the feedstock, the remaining stream that will be hydrolyzed has only 14.6 wt.%cellulose and 8.9 wt% hemicellulose, dry basis.

In the washing step a stream with diluted sulfuric acid wash the pulp and remove the sugar degraded products that act as inhibitors for the fermentation process and the calcium carbonate and sodium hydroxide that act as inhibitors for the enzyme activity. During the washing step is also considered that a pH adjustment is made. The optimal pH for the activity of the microorganisms is around 4.5 [\[90\]](#page-62-6).

3.3.3 Area 300: Enzymatic hydrolysis

In this area takes place the conversion of cellulose and hemicellulose into glucose and xylose, respectively, through enzymatic activity. Cellulase enzymes can be described as a solution with a mixture of enzymes that convert the biomass fibers into sugars. The process design in this project is known as separate hydrolysis and fermentation (SHF), the reason to use this process is that it allows each of the processes to take place at the optimal temperature and enabling batch processes [\[91\]](#page-62-7). According to Olsson et al., 2006 [\[92\]](#page-62-8), the optimal temperature for the enzymatic hydrolysis is 50^0 C. Figure [7](#page-25-1) presents a scheme of the enzymatic hydrolysis process.

Figure 7: Scheme of the designed Area 300 - Enzymatic hydrolysis.

The washed pulp is transferred to a solid loading adjustment tank (V-301) by the pulp belt conveying

(BC-301). In this tank, the pulp is diluted to guarantee a solid loading of 20wt.%, this decision is linked with the steps done in the pretreatment section to avoid a high concentration of inhibitors and to allow a good mass transfer. A pump (PM-301) is in charge to drive the stream to a heater (HX-301) where the temperature is adjusted to 50^0 C. After that, the enzymes are mixed with the stream in a relation of $20mg$ enzymes to 1g of fibers (cellulose and hemicellulose) following the proportion used in Humbird et al., 2011 [\[78\]](#page-61-1).

The enzymatic hydrolysis process is projected as a batch process because of its low investment cost and wide use in the ethanol industry [\[93\]](#page-62-9), to keep a continuous process it is needed to have multi-staged units. The same principles are applied to the design of the batch seed fermentation and fermentation processes. The hydrolysis process has a residence time of three days, based on the experiments from Teater et al., 2011 [\[36\]](#page-58-16) and also in the analysis made by Humbird et al., 2011 [\[78\]](#page-61-1). The conditions of the hydrolysis process are presented in Table [8.](#page-26-1) Table [9](#page-26-2) presents the enzymatic hydrolysis reactions and assumed conversions, based on Humbird et al., 2011 [\[78\]](#page-61-1) and Kumar et al., 2011[\[89\]](#page-62-0). After 72 hours, the hydrolyzed stream (S-306) is transferred from the enzymatic hydrolysis process to the fermentation process [\[78\]](#page-61-1), [\[89\]](#page-62-0).

Table 8: Enzymatic hydrolysis conditions.

3.3.4 Area 400: Fermentation

The role of the fermentation process is to ferment the sugars obtained from the enzymatic hydrolysis process in ethanol. First, to avoid the inhibitory effects of lignin on the yeasts [\[94\]](#page-62-10), a solid/liquid separation step is conducted by another rotary vacuum filtration (RVF-401). The cake obtained in this process, rich in lignin, follows to the boiler area where it will be burned. On the other hand, the filtrate goes to the cooling where the optimum yeasts work temperature, 30^0 C, is adjusted to the stream [\[95\]](#page-62-11). After that, the filtrate stream $(S-402)$ is separated in a ratio of $10/90$, where $10v/v\%$ of the stream is mixed with sources of nitrogen (corn steep liquor - CSL) and phosphorus (diammonium phosphate - DPA) an directed to a seed fermentation tank (SFR-401) where the inoculate solution is fermented to provoke the growth of the yeasts, the microorganism that ferments the sugars. In the simulation, process yeast has the same composition as glucose $(C_6H_{12}O_6)$. The seed fermentation process is done in a batch process with multi-staged reactors to keep producing yeasts to the continuous process. The residence time of the seed fermentation is one day [\[78\]](#page-61-1). Table [10](#page-27-1) summarizes the seed fermentation conditions and Table [11](#page-27-2) shows the reactions occurring during the seed fermentation process, [\[78\]](#page-61-1). Figure [8](#page-27-0) shows a scheme of the fermentation process.

Area 400 - Fermentation

Figure 8: Scheme of the designed Area 400 - Fermentation.

Table 10: Seed fermentation reactor specifications.

Table 11: Seed fermentation reactor reactions.

Reaction	Reactant %Converted to yeast
$nGlucose \rightarrow nYeast$ Glucose	97
$nXylose \rightarrow nYeast$ Xylose	97

The fermentation process continues with the mixing of the broth (S-404) and the seed (S-413) streams in the fermentation tank, that also will occur in a batch process with multi-staged units at 300C. Table [12](#page-27-3) present the features of the fermentation reactor and Table [13](#page-28-2) presents the reactions to convert the sugars into ethanol. After the fermentation step, the stream is driven to the separation and purification of ethanol.

Table 12: Fermentation conditions.

Temperature	30° C
Residence time 2 days	
	Inoculum level $10 \text{ vol}\%$ of production vessel size

3.3.5 Area 500: Separation and purification

In this step the separation of the stream into anhydrous ethanol (99,5% purity), water, and non-fermented components occurs. Distillation and molecular sieve adsorption are used to recover ethanol from the raw fermentation stream and produce a stream with 99.5% ethanol, which is the main product of the process. One distillation column is used to separate the non-fermented components and most of the water of the feed stream. The distilled stream leaves the column and it is further dehydrated to 99.5% by a molecular sieve equipment. After the molecular sieve, the anhydrous ethanol stream is cooled down and stored. The non-fermented components and water from the distillation column and the residues from the molecular sieve are directed to the wastewater treatment. Figure [9](#page-28-1) presents the separation and purification process.

Area 500 - Separation and purification

Figure 9: Scheme of the designed Area 500 - Separation and purification.

The distillation column used in this step (C-501) is simulated in SuperPro using a rigorous model based on Modified Raoult's Law with Wilson coefficients, this method was used because the ethanol-water mixture forms an azeotrope, where ethanol cannot be completely purified [\[96\]](#page-62-12). Table [14](#page-28-3) presents the main features of the distillation column.

The distillate leaves the column and is pressurized by a molecular sieve pump (PM-501) and heated until to be superheated in the heater (HX-501). When the stream reaches the molecular sieve (CSP-501), water is selectively adsorbed in the beds as the vapor flows through and the 99.5% pure ethanol vapor is cooled down by a heat exchanger (HX-502) and directed to the storage (V-501).

3.3.6 Area 600: Evaporator, boiler, and turbogenerator

The evaporator, boiler, and turbo-generator area have the purpose of burning the organic by-products streams to make the plant self-sufficient in energy and steam ("thermal-neutral"). Combustible by-products composition include lignin and the uncovered cellulose and hemicellulose from the feedstock, as well as the biogas produced in the wastewater treatment. Other advantages of this process are to reduces solid waste disposal costs, and generate additional revenue through the sale of potential excess electricity and heat. Figure [10](#page-30-0) shows a scheme of the evaporator, boiler and turbogenerator area.

The streams from the Area 100 and Area 400 have an expressive concentration of organics left from the process. They are received in a lignin blending tank (V-601) and are directed to the evaporator by the pump (PM-601). After that, the stream is preheated by the output vapors that leave the evaporator in the heat recovery (HX-603). The evaporation step is needed because the steam generator only can handle fuels with a maximum of 60wt.% moisture [\[97\]](#page-62-13). In this project, the fuel admitted in the boiler leaves the evaporator with 40% moisture, to reach a better performance.

In the evaporator is a 3-effect-evaporator (EV-601) using mechanical vapor recompression. The vapor follows to exchange heat with the incoming fuel and is cooled down to return to the process in the form of liquid water (S-626, S-627, and S-628). The fuel is mixed with the biogas stream that came from the wastewater treatment, and it is directed to the boiler (SG-601). Due to the combustion of the fuels, an input stream of saturated liquid water is superheated to 450 °and 65 bar, following the actual conditions at twence, and it is directed to the turbine (ET-601). Flue gases and ashes also leave the boiler.

The turbine/generator (ET-601) is an extraction turbine that generates energy and steam for all the process. After to be decompressed the steam that left the turbine is mixed with the steam used in the process and goes to a condenser (HX-602), where the heat is used to district heating and, the saturated water is redirected to the boiler (S-614).

3.3.7 Area 700: Wastewater treatment

Streams from pretreatment and separation areas are pumped to the wastewater treatment. The purpose of this treatment is to recondition the water to the process and also produce biogas to be used in the steam generator system. Figure [11](#page-31-1) present a schematic draw of the wastewater treatment process. Table [15](#page-31-2) present the reactions that happen in the wastewater plant to produce biogas. In this project, the wastewater treatment is treated as a black-box (GBX-701) to simplify the analysis.

Figure 11: Scheme of the designed Area 700 - Wastewater treatment.

3.3.8 Considerations about the optimized version

For the second scenario, the ethanol plant uses the facilities that Twence B.V. has already. In this case, the Area 600 is partially suppressed; only the evaporator is kept to provide fuel more concentrated to Twence's boiler. Moreover, Area 700 is totally suppressed, which means that the wastewater treatment will be completely done at Twence's actual structure. In Figure [12](#page-32-3) it is possible to verify the schematic draws with the changes for Area 600 due to the optimized version.

Figure 12: Scheme of the designed Area 600 - Evaporator, boiler and turbogenerator (optimized version).

3.4 Economics

The economic evaluation of the project considers the cost estimation for the year 2018 and that the plant will be built in the Netherlands. As the majority of the costs are in US dollars, all the values were converted to Euros using the average of the currency exchange during 2018, which is $1USD = 0.8475EUR$ [\[98\]](#page-62-14). For the economic evaluation of the project, two scenarios were done; the grass-root scenario and the optimized scenario, as explained before.

3.4.1 Estimation of the capital investment

The capital investment to build the designed process plant is estimated based on the Overall Factor Method of Lang [\[99\]](#page-62-15),[\[100\]](#page-62-16),[\[101\]](#page-62-17). The accuracy of this method is $\pm 35\%$.

With the mass and energy balances and the equipment sizing, the f.o.b. equipment cost, C_P can be estimated. Using Equation [1](#page-32-4) the total capital investment, C_{TCI} was obtained.

$$
C_{TCI} = 1.05 f_{LTPI} \sum_{i} (I_i/I_{bi}) C_{pi} \tag{1}
$$

The factor 1.05 takes into account the delivery of the equipment to the plant site. The Lang factor f_{LTPI} used in this work is 5.60, and the detailed breakdown of the Lang factors can be seen in the Appendix A. I_i stands for the index cost of the year of the project and I_{bi} is the cost index for the base year. For the estimations in this project, the index cost is The Chemical Engineering (CE) Plant Cost Index, the values CE used are presented in Appendix B.

The cost of land was estimated as 2% of the total depreciable capital cost, and the location factor 1.2 was applied for installation in western Europe, both assumptions are based on Seider et al., 2010 [\[85\]](#page-62-2).

3.4.2 Estimation of the variable operating costs

With the mass and energy balances, it is possible to calculate how much is spent every year with variable operating costs such as utilities, chemicals, and so on. Table [16](#page-33-2) present the variable operating costs per unit used in this project updated to 2018 and the source of the value. The feedstock cost will be estimated as zero for the grass-root scenario. According to Adriaansn et al., 2019 [\[40\]](#page-59-3), the farmers need to pay to give a destiny for the digestate in the range of ϵ 3-25.

Component	Cost(2018)	Source
Feedstock	$\in 0/\text{kg}$	[102]
Utilities		
Steam, 50 psig	€8,83/MT	[85]
Electricity	€0.051/kWh	Twence
Cooling water	€0.0267/m ³	[85]
Chilled water	€5.35/GJ	[85]
Landfill	€0.07/drykg	Twence
Wastewater treatment	€0.44/kg organic removed	[85]
Chemicals		
Sodium hydroxide	€0.59/kg	$\left[103\right]$
Sulfuric acid 93%	€0.10/kg	[103]
DAP	€0.34/kg	$\left[103\right]$
CSL	€0.17/kg	$\left[104\right]$
Cellulase	€0.68/gal ethanol produced	$\left[105\right]$

Table 16: Utilities and chemical costs and sources

3.4.3 Estimation of the fixed operating costs

The fixed operating costs are the costs that are independent of the production of the process. To calculate the fixed operating costs, the number of the operator need to be determined. An estimation for the number of operators per shift used in Twence B.V. is 0.1 operator per shift per equipment. Applying this methodology, a number of 6 operators per shift is needed for the grass-root scenario and four operators per shift in the optimistic scenario. The wage applied in Twence B.V. for the operators is ϵ 55.000,00 per year. The methodology to estimate the other fixed operating costs is based on Seider et al., 2010 [\[85\]](#page-62-2). Table [17](#page-34-2) shows how the other operating costs are estimated, the annual cost of manufacture is giving by the sum of the feedstock, utilities, chemicals operations, maintenance, operation overhead, property taxes, and insurance and depreciation. In Table [17](#page-34-2) DWB stands for Direct wages and benefits; C_{TDC} is Total depreciable capital; MWB: maintenance wages and benefits; MO-SWB: maintenance and operations salary, wages, and benefits; and, C_{alloc} : allocated costs for utility plants and related facilities.

Operations		
Direct salaries and benefits	15%	of DWB
Operating supplies and services	6%	of DWB
Technical assistance to manufacturing	ϵ 60.000,00	$(operator/shift)-year$
Control laboratory	ϵ 65.000,00	$(operator/shift)-year$
Maintenance (M)		
Wages and benefits		
Solid-fluids handling process	3.5%	of CTDC
Salaries and benefits	25%	of MWB
Materials and services	100%	of MWB
Maintenance overhead	5%	of MWB
Operating overhead		
General plant overhead	7.1%	of MO-SWB
Mechanical department services	2.4%	of MO-SWB
Employee relations department	5.9%	of MO-SWB
Business services	7.4%	of MO-SWB
Property taxes and insurances	8\%	of C_{TDC}
Depreciation	2%	of C_{TDC} -1.18 C_{alloc}

Table 17: Fixed operating costs sheet

3.4.4 Estimation of the general expenses

General expenses comprise five categories: selling (or transfer) expense, research (direct and allocated), administrative expense, and management incentive compensation; these costs are based on [\[85\]](#page-62-2). Table [18](#page-34-3) presents how these expenses are calculated; the total general expenses is given by summing the values related to the general expenses. Also, the total production cost results from the sum of the cost of manufacture and the total general expenses.

Table 18: General expenses sheet.

General expenses	
Selling (or transfer) expense	1% of sales
Direct research	4.80% of sales
Allocated research	0.50% of sales
Administrative expense	2.00% of sales
Management incentive compensation 1.25% of sales	

3.4.5 Estimation of the total sales

The estimation of the value of the total sales is a consequence of the products and by-products sold by the plant for this project the anhydrous ethanol and the by-products are electricity and steam. Table [19](#page-35-0) present the values used to sell these products.

Table 19: Sales sheet

Sales		
Anydrous ethanol ϵ 466.11 ϵ /cbm		[106]
Electricity	$\in 0.05 \in /kWh$	Twence
Steam	\in 8.93 \in /MT	[85]
4 Results and discussion

4.1 Ethanol production

The anhydrous ethanol production of the designed plant is 551 kg/h. This ethanol contains 99.5% pure ethanol and 0.5% water. Table [20](#page-36-0) presents the leading products and by-products obtained by the designed biochemical process as well as the consumption of steam and electricity. The idea to present this Table is to help the reader to understand some of the comments made during the analysis of the results. The values will be commented in the next sections. For both scenarios, grass-root and the optimistic, the carbon, energy, and water balances are the same.

Table 20: General results obtained from the designed project - grass-root and optimistic scenarios.

4.1.1 Carbon balance

Overall mass and energy balances were performed using the SuperPro model. Table [21](#page-36-1) shows the flow of carbon inputs and outputs, carbon outlet reached 99.7% of the initial flow; this is due to the rounded values adopted. Most of the carbon in the process is from the feedstock, with just a small amount coming from the cellulase.

The major output of the carbon flow is in the form of carbon dioxide exhaust from the combustion (76.5%), and 12.5% of the carbon leaves the system as ethanol. From all the carbon present in the feedstock, 47% is in the form of cellulose and hemicellulose and from this percentage, only about one quarter is converted to ethanol. Comparing with the results from Aden et al., 2002 [\[107\]](#page-63-0), where the feedstock (corn stover) consist of 64.2% ethanol-producing reactants and the conversion reaches 33.9%, and with Humbird et al.,2011 [\[78\]](#page-61-0) where 29.2% of the carbon is converted to ethanol, the carbon conversion in this project is less than the half of them. This is caused by the relatively low content of carbohydrates in SPD and also because of the glucose and xylose losses during the washing step in the pretreatment, 38% and 49% respectively. The remaining carbon flow leaves the system as carbon dioxide from the fermentation process 6.4% and as wastewater slurry, 3.9%

For the optimistic version of the project, there is no difference to the grass-root scenario in terms of carbon balance. Therefore, the carbon flow that leaves the system to Twence's boiler has the same content as the combustion exhaust of the grass-root project, the same happening for the wastewater slurry.

4.1.2 Energy balance

An energy balance was performed to compare the energy products from the process (ethanol, district heating, and electricity) to the potential energy in the biomass feed. The lower heating value is used to compare the major streams produced by the ethanol plant because it is more accurate than to use the higher heating value, because it does not consider the heat from steam condensation. Table [22](#page-37-0) shows the energy balance using the system as the volume control.

Table 22: Ethanol plant overall energy balance

As it can be seen in Table [22](#page-37-0) only 17.3% of the all energy content in the feedstock is converted to ethanol, and the overall efficiency of the system is 45.2%. The equations for the efficiency calculations are given in Appendix C - Efficiency equations, based on the work done by Lind et al., 2010 [\[108\]](#page-63-1).

To compare the efficiency obtained with other projects a graph is plotted in Figure [13](#page-38-0) considering in the x-axis the biomass-to-fuel efficiency, η_{btf} , and in the y-axis the thermal efficiency of the system, η_{th} . It is possible to verify that the designed project is a bit far for the delimited ethanol production, again the main reasons for such a low efficiency are the poor content of carbohydrates in the feedstock and the losses of sugars during the pretreatment.

Figure 13: Biorefinery efficiencies comparison, project pointed with the black arrow, adapted from Lind et al., 2012 [\[108\]](#page-63-1)

4.1.3 Water balance

Water consumption is considered high in the biochemical conversion of biomass when compared with the thermochemical conversion or even for a petroleum-based fuel [\[78\]](#page-61-0). Table [23](#page-39-0) shows the water balance for the designed project. In order to compare with other studies it is used 24.1 l of water per kg ethanol produced, which is high when compared with Humbird et al., 2011 [\[78\]](#page-61-0) and the dilute alkali process of Kumar et al., 2011 [\[89\]](#page-62-0) 6.3 l and 7.72 l/kg of ethanol. The reason is the washing step after the pretreatment reactor to avoid that sodium hydroxide reaches the hydrolysis process. To minimize the effects of the high water consumption, the system was designed to recover it from the evaporator to the system and also from the wastewater treatment to the system. Then, taking into consideration this closed-loop, the water that leaves the system is equal to the water that comes with the feedstock.

Overall water balance in the system (kg/h)				
Input		Output		
Feedstock	13258	Wastewater recovery (S-707/S-708)	23667	
First dilution (S-108)	9470	Evaporator recovery $(S-626/S-627/S-628)$	17344	
Second dilution (S-110)	5018	Ethanol $(S-506)$	3	
Sodium hydroxide (S-208)	511	Exhaust gases (S-619)	5841	
Washing $(S-213)$	23431	Steam $(S-614)$	18342	
Steam $(S-618)$	18342	Pretreatment reactor	122	
Seed fermentation	11	Hydrolysis consumption	138	
Steam generation	2571	Rejected water (S-709)	7153	
Total	72612	Total	72612	

Table 23: Ethanol plant overall water balance

4.1.4 Cost analysis - grass-root scenario

The mass balance presented in Appendix D it was possible to calculate the f.o.b. cost of the pieces of equipment used in this process, the results are presented in Appendix E. The total capital investment, calculated according to the Lang factor presented in Appendix A, is showed in Table [24.](#page-40-0) It is possible to verify that the main cost of process equipment is from the Area 600, that comprises the boiler, turbine and the evaporator, that is responsible for providing service facilities for the entire plant, and as commented by Seider et al., 2010 [\[85\]](#page-62-1) can be substantial for a grass-root plant. After that, Area 200 has a high cost, and the main responsible for that is the rotary vacuum filtration (RVF-201) and the pretreatment reactor (R-201), which are the most robust equipment in the section. The other areas have the delivered cost in the range of $0.7 - 1.2M \in .$

The resulting Lang factor (fixed capital investment/purchase cost) 3.73 is a higher value than other similar ethanol plants, as 3.2 reached by Davis et al., 2013 [\[109\]](#page-63-2) or 2.98 reached by kazi et al., 2010 [\[110\]](#page-63-3), mainly because the factors used for them are less conservative. Besides that, no factor was specified for services, since the process already presents the structure to provide the facility services.

Table 24: Total capital investment for the second generation ethanol plant (grass-root scenario)

With the mass balance, it was also possible to calculate the variable operating costs. The calculations of the electricity, steam, and cooling water can be checked in !!!Appendix F!!!.

Table [25](#page-42-0) shows the cost sheet of this project, and Figure [14](#page-41-0) present the shares of the cost according to the group of costs. It is considered that the cost to obtain the feedstock is zero. According to Adriaansn et al., 2019 [\[40\]](#page-59-0) farmers need to pay to dispose of the solid part of the digestate from ϵ 3 to 25 per ton.

Steam and electricity are produced with the combustion of the by-products of the plant. For the supply of cooling water and chilled water, it was decided that it is more beneficial for the project to purchase them, instead of building the facilities, due to the low consumption of these services.

Among the chemicals the most costly is the sodium hydroxide reaching ϵ 2400k per year. It is a common practice to recover it in the pulp and paper industry during the Kraft process. However, the application of the sodium hydroxide recovery in the dilute alkali process is still not possible. The level of delignification required for ethanol production is low, and this reduces the organic substances extracted, and, also, due to the extensive washing steps needed, too much energy will be necessary to evaporate the water [\[111\]](#page-63-4). Besides that, the estimated capital cost of sodium hydroxide recovery may exceed the total equipment cost of a biorefinery [\[62\]](#page-60-0).

Figure 14: Grouped costs of the second generation ethanol plant for the grass-root scenario.

Another high chemical cost is cellulase. Alternatives to decrease this cost are recycling and on-site production. The recycling presents issues with the stability of enzymes and their adsorption to residual biomass [\[112\]](#page-63-5), and, cellulase production affects sensibly the availability of cellulose for the ethanol production [\[78\]](#page-61-0), which for this design process is a problem, since the feedstock has already low cellulose content comparing with agriculture residues, for instance.

Depreciation of the pieces of equipment was consider for 10 years, and it is a higher cost for the project and only can be decreased with decreasing the capacity of the plant, which will decrease the production and also the yields, or with improvements in the system with the adoption of different technologies.

The operation costs are relevant costs inside the cost sheet, this is due to the number of operators per shift, this project does not detail how automated is the production, but due to the specificity of the different process, six operators per shift is the minimum amount of operators needed. The technical assistance to manufacturing and the control laboratory are related to the number of operators per shift. Maintenance costs are also among the high costs, but they are directly influenced by the fixed capital investment.

The ethanol production and the sales of the by-products electricity and steam are not able to cover the expenses to maintain the production of ethanol. The main reasons for the low production of ethanol that can be mention are: the content of cellulose and hemicellulose is low when compared with other waste feedstocks. This happens because the carbohydrates were consumed by the two digestion processes before the biorefinery. Another reason for that is the losses due to the pretreatment and subsequent washing step, cellulose and hemicellulose are already hydrolize during the pretreatment and how the dilute alkali process need a washing step of the fibers after pretreatment to avoid the presence of sodium hydroxide in the enzymatic hydrolysis process, the sugars formed are lost and directed to the steam generation.

Although it is not the main product of this project, electricity revenues could help the feasibility of the production. Electricity production is also affected by the low content of fibers in the feedstock that will be the fuel for steam generation; and by the low solid loading needed to avoid the high viscosity on the flows which result in high consumption of energy for the evaporation process. Agitation of the tanks also has a high energy consumption; this is mainly due to the composition of the streams that require more power to mix and also due to the large volumes that need to be kept in the batch reactors for days in the hydrolysis and fermentation processes. The consumption of steam is another reason why electricity production is not higher; steam needs to be extracted from the turbine at 5 bar and 152 °C to feed the heated processes. The steam production is resulting in the rejected steam that cannot produce work anymore; this will be sold to provide district heating.

With this designed grass-root scenario, unfortunately, it is not worth to evaluate a cash flow analysis. The costs of production are 5.2 times higher than the sales revenue, this happens because of the low productivity of the ethanol and also because the high capital investment and the price of chemicals, mainly sodium hydroxide and cellulase.

In the Netherlands the companies that deliver renewable energy, from certain feedstocks that includes

lignocellulosic biomass, to the Dutch transport market are recompensed with a subside called hernieuwbare brandstofeenheden (HBE) [\[113\]](#page-63-6). According to Twence B.V., for the ethanol produced this subside is about ϵ 330 per tonne. If HBE is considered the relaion between the cost of production of ethanol and the revenues fall to 3.45, but still the sales do not overcome the cost of production. Therefore, an alternative scenario is explored in the next subsection using some of the facilities already available in Twence.

Table 25: Project cost sheet for the grass-root scenario

Cost sheet outline Cost Factor Cost (ϵ) Unit/based cost Source Stream (unit/h) Total/h Total(ϵ)/year Feedstock $\overline{\epsilon}0$ per kg 18940 $\overline{\epsilon}$ **Utilities** Cooling water $\epsilon_{0.03} \epsilon/m^3$
Chilled water $\epsilon_{5.35} \epsilon/GJ$ $[85]$ 105 $\in \{2.81$ 20k Chilled water $\epsilon_{5.35} \epsilon/GJ$ [\[85\]](#page-62-1) 0 ϵ_{-} Landfill ϵ 0.07 per dry kg Twence (2018) 1981 ϵ 138.66 1100k Chemicals Sodium hydroxide ϵ 0.59 per kg [\[103\]](#page-62-2) 510.86 ϵ 303.06 2400k Sulfuric acid ϵ 60.10 per kg [\[103\]](#page-62-2) 62.4 ϵ 6.35 50k DAP $\epsilon 0.34$ per kg $[103]$ 6 $\epsilon 2.03$ 20k ϵ CSL enterprise that ϵ 0.17 per kg in $[114]$ 44.8 ϵ 7.59 60k CSL CSL ϵ 0.17 per kg [114] 44.8 ϵ 7.59 60k
Cellulase ϵ 0.68 per gal ethanol produced [\[105\]](#page-63-8) 184.92 ϵ 125.37 990k **Operations** Direct wages and benefits (DW&B) ϵ 34.72 \$/operator-hour Twence (2018) 6 ϵ 208.32 1650k
Direct salaries and benefits 15% DW&B 0.90 ϵ 31.25 250k Direct salaries and benefits 15% DW&B 0.90 ϵ 31.25 250 0.90 ϵ 31.25 250 0.90 ϵ 31.25 Operating suplies and services 6% DW&B 0.36 €12.50 100k

Technical assistance to manufacturing €60,000.00 (operator/shift)-year Twence (2018) - - 360k $\begin{tabular}{lccccccc} Technical assistance to manufacturing & $\text{\textcircled{\textless}} 60,000.00$ & (operator/shift)-year & Three (2018) & - & - & - & 360k\\ Control laboratory & & $\text{\textcircled{\textless}} 65,000.00$ & (operator/shift)-year & Three (2018) & - & - & - & 390k\\ \end{tabular}$ $(operator/shift)$ -year Maintenance (M) Wages and benefits (MW&B) Solid-fluids handling process 3.50% of CTDC 1290k Salaries and benefits 25% of MW&B 320k
Materials and services 200% of MW&B 320k
290k Materials and services 100% of MW&B $1290k$ Maintenance overhead 5% of MW&B 60k Operating overhead General plant overhead 7.10% of M&O-SW&B 210k Mechanical department services 2.40% of M&O-SW&B 70k Employee relations department 5.90% of M&O-SW&B 170k Business services 7.40% of M&O-SW&B 220k Property taxes and insurance 2% of CTDC 8% of (CTDC-1 18Calloc) $2530k$ $\underline{\begin{array}{c} 2530\mathrm{k}\\ 14290\mathrm{k} \end{array}}$ COST OF MANUFACTURE (COM) General expenses Selling (or transfer) expense $\frac{1\%}{4.80\%}$ of sales $\frac{30k}{4.80\%}$ of sales $\frac{130k}{4.80\%}$ Direct research 130k 4.80% of sales 130k Allocated research 0.50% of sales $10k$ Allocated research 0.50% of sales 1.25% of sales $40k$
Administrative expense 2.00% of sales $40k$
Management incentive compensation 1.25% of sales Management incentive compensation 1.25% of sales 40k
 TOTAL GENERAL EXPENSES (GE) 270k TOTAL GENERAL EXPENSES (GE) TOTAL PRODUCTION COST (C) 14560k **Sales** Anydrous ethanol ϵ 466.11 per ton [\[103\]](#page-62-2) 0.551 ϵ 256.83 2030k Electricity euro 0.051 per kWh/h Twence(2018) 244.57 ϵ 12.44 100k District heating ϵ 10.00 per MWh/h [\[85\]](#page-62-1) 8.6 ϵ 86.00 680k **TOTAL SALES** 2810k

4.2 Optimistic scenario

For this optimized scenario some of the facilities that already exist at Twence are used in order to decrease the fixed capital cost and the related costs, another consideration is that the farmers pay to the company to handle the feedstock, this assumption is based on [\[40\]](#page-59-0)., Then, the assumption is that the farmers are charged in ϵ 25 per ton, discounting the transportation costs, ϵ 10 per 100km and considering that in a radius of 50km is enough to reach the needed feedstock, the revenue from the feedstock is $\in 20$ per tone of the solid part of the digestate. The consequences of these changes are: the reduction of the number of operators since less equipment are needed for the process five workers are designated per shift. Also, an assumption is that Twence will not charge the ethanol plant to provide steam, electricity, wastewater treatment, and to

landfill the residues of the process. Table [26](#page-43-0) shows the total capital investment for this optimistic scenario. Comparing with the grass-root scenario, the only cost addressed to the area 600 is the evaporator, and no investment is destinated to the wastewater treatment area. Because of that, the total capital investment reduced from ϵ 55.4M to ϵ 33.7M, which will reflect in the costs of production.

Delivered cost of process equipment	Cost (ϵ)
Area 100: Front-end operations	.640M
Area 200: Pretreatment	1.880M
Area 300: Hydrolysis	1.130M
Area 400: Fermentation	.920M
Area 500: Separation	.560M
Area 600: Evaporator	.900M
Area 700: Wastewater treatment	.000M
Total	6.030M
Installation	2.350M
Instrumentation and control	1.570M
Piping	1.870M
Electrical	.600M
Buildings (including services)	1.750M
Yard improvements	.720M
Service facilities	.000M
Total direct plant cost	14.890M
Engineering and supervision	1.930M
Construction expenses	2.050M
Total indirect plant cost (TIC)	18.870M
Contractor's fee and legal expenses	1.390M
Contingency	2.230M
Fixed capital investment (FCI)	22.490M
Cost of land	.380M
Cost of plant start-up	1.490M
Total permanent investment	24.360M
Investment site factor	
(Western Europe)	4.870M
Working capital	4.523M
Total capital investment	$\overline{3}3.750\mathrm{M}$
Lang factor (FCI/purchase cost)	3.73
Lang factor (TCI/purchase cost)	5.60

Table 26: Total capital investment for the second generation ethanol plant (optimistic scenario)

Figure [15](#page-44-0) present the grouped costs for the optimistic scenario and Table [27](#page-44-1) presents the cost sheet for the optimistic version. Comparing the two cost sheets it is possible to verify that the utilities cost is higher in the green-field project because of the cost of the landfill the inorganics, and this is not counted in the optimistic scenario. For the chemicals, no difference in costs can be verified.

In the operations there is a reduction because fewer operators are needed and maintenance and operating overhead costs decrease because of fewer operators in the process and also because the fixed investment is lower due to fewer pieces of equipment are needed in the optimistic scenario. Depreciation and property taxes and insurance diminish because they are based on the fixed investment. The values for general expenses increased in the optimistic scenario because they are based on the sales.

Overall, the relation between the total production costs to the total sales is 2.14 to the optimistic scenario, which is an improvement considering the grass-root scenario, but still far to cover the production cost. Also,

considering HBE the relation between production costs and sales is 1.62, the best relation found for this project, however still not feasible.

Figure 15: Grouped costs of the second generation ethanol plant for the optimistic scenario.

Another assumption from the optimistic scenario is to consider that Twence B.V. will charge the steam,

electricity and landfill for the ethanol company. This situation also was taken into account, for that it was considered that the price of steam per ton is $\epsilon 4.90$ per ton, the price of electricity is $\epsilon 0.025$ per kWh/h and the price of the landfill is 0.0035 per dry kg. These costs are about half of the price that is charged in the market. The other utilities as cooling water and chilled water are not considered since they are not significant and the waste water treatment will not be charge because of the biogas and energy that can be produced from it. This will increase the difference between the cost of production and the sales to $7010k\epsilon$ and the cost of production will be and the relation of these costs to 2,39.

Table [28](#page-45-0) presents a survey of some techno-economic analysis for the different ethanol plants, using different feedstocks and pretreatment methods, where MESP stands for minimum ethanol selling price; this value is achieved through the cash flow analysis. Due to the cost of production be higher than the sales revenue an analysis of the MESP will not be done in this project. Besides that, the MESP of the other projects is compared with the cost of production of this project, as mentioned in [\[78\]](#page-61-0) the cost of production is lower than the MESP value.

The cost of production per gallon of ethanol is calculated taking in consideration the total annual cost of production minus the revenues from feedstock, for the optmistic version, or the revenues from electricity and district heating for the grass-root scenario. This result should be divided by the annual production of ethanol. For the optimistic version the cost of production is ϵ 5.40/gal and for the grass-root version is ϵ 9.50.

In addition, the values presented in Table [28](#page-45-0) are not updated to 2018, they are just converted from American dollars to euros, using the average exchange rate from 2018 [\[98\]](#page-62-3). This comparison is done to present how similar is this project to other projects in terms of scale, feed price and ethanol yield.

Considering the limitations of the comparisons, it is possible to extract from the Table [28](#page-45-0) that the calculated cost of production in this project is quite variable, this happens because the revenues from the feedstock increase the sales value significantly. Comparing the obtained value with the other projects it is possible to verify a significant difference, even for the optimistic scenario, this happens because SPD has low content of

carbohydrates, moreover there are losses of them during the process. Another reason that needs to be further investigated is the effect of economy of scale in this project, since the comparison is done with projects that handle, an average of ten times more dry tons per day.

Moreover, the advantage to use this feedstock is the possibility to get revenues from that, which is not possible in the mentioned projects. Also, the ethanol yield per dry ton relation is lower for the SPD project in comparison with the other projects, this also is a consequence of the low carbohydrate content in SPD and the carbohydrates that are not converted to ethanol during the process.

4.3 Sensitivity analysis

In this section, a sensitivity analysis is done with the techno-economic model used for the optimistic version. For that, the conversion parameters were increased and decreased 20% from the initial value, and the difference in cost and revenues, as well as, the ethanol yield were investigated. Table [29](#page-46-0) presents the assumptions varied in the sensitivity analysis.

Table 29: Assumptions varied in the sensitivity analysis

Figure [16](#page-47-0) and [17](#page-47-1) shows the results of the sensitivity analysis for the difference between the annual cost and annual sales and ethanol yields, respectively. The base case (0) for Figure [16](#page-47-0) is the production of ethanol for the parameters presented in section 3, and for Figure [17](#page-47-1) is the difference of annual production cost and sales, as showed in Figure [27.](#page-44-1)

In Figure [16](#page-47-0) it is possible to verify that the factor that most influences the production of ethanol is the conversion of the cellulose to glucose during the pretreatment, showing that the losses of cellulose are very harmful for the process. Unfortunately, the washing step is needed to get rid off calcium carbonate and sodium hydroxide in the pulp, but some references claim that cellulose and hemicellulose should not be solubilized in dilute alkali process, perhaps this fact should be better investigate [\[69\]](#page-61-1), [\[22\]](#page-58-0). Besides that, it can be verified that the changes in the conversion of cellulose affect more the yields of ethanol than the changes in the conversion of xylose, this is a direct consequence of the higher content of cellulose than xylose in the feedstock.

On the other hand, the decrease in the conversion of cellulose during the enzimatic hydrolysis process and the decrease of the conversion of glucose during the fermentation are the most harmful effects for the ethanol production, which means that the hydrolysis and fermentation are very sensible processes, taking into account that the microorganisms need to be in specific conditions to survive, these are very unstable parts of the system.

In Figure [17](#page-47-1) it was considered that the changes in the ethanol production will not change the equipment sizing, then the changes in the values are a direct consequence of the increase or decrease in the sales. However, it can conclude from Figure [17](#page-47-1) that even the increase or decrease in the conversion do not affect significantly the relation between costs and sales to the point of increase the feasibility of the process.

Figure 16: Sensitivity analysis of ethanol production varying the conversion in the reactions in the process, yields in kg/h. The base case is represented by 0 which correspond to a production of 551 kg/h of ethanol.

Figure 17: Sensitivity analysis of the difference between the annual cost and sales in ϵ k varying the conversion in the reactions in the process. The base case is represented by o which correspond to a difference between annual production cost and annual sales revenue of 5760k \in .

5 Alternative for the solid part of the digestate for energy production

As the lignocellulosic ethanol production does not seem to be a profitable option for the use of the solid part of the digestate, further development needs to be done. Other options need, thus, to be explored. One of the options that may bring some synergy with the business model of Twence is pyrolysis. It is also a field where still some research needs to be done, but according to the researches done, [\[123\]](#page-64-4), [\[124\]](#page-64-5), [\[125\]](#page-64-6), [\[126\]](#page-64-7), [\[127\]](#page-64-8), [\[128\]](#page-64-9), [\[129\]](#page-64-10) and [\[130\]](#page-64-11) it seems to be possible to integrate the anaerobic digestion process with pyrolysis. This section aims to analize an alternative process for energy production, using SPD as feedstock. Moreover, to evaluate from a techno-econmic point of view, which the drawbacks and advantages of these technologies in comparison with ethanol production are.

5.1 Solid part of the digestate in the circular economy

Circular economy can be defined as an economic system where products and services are traded in closed loops, and it aims to create a system that allows for the long life, optimal reuse, refurbishment, remanufacturing and recycling of products and materials [\[131\]](#page-64-12). Figure [18](#page-48-0) presents a scheme that shows the circular economy of the organic waste that uses anaerobic digestion to produce biogas as fertilizer. SPD can be inserted in the circular economy context in many initiatives; some examples are the agriculture application as a fertilizer [\[132\]](#page-64-13), the recovery of macronutrients (N,P.K) and micronutrients (MG, S, Ca, B, Cu, Co, Mn and Zn) that can serve as raw material for the chemical industries [\[133\]](#page-64-14), production of bioproducts, as enzymes, bioplastics and biopesticides [\[134\]](#page-64-15) and, construction materials as fibreboards (MDF) and wood-plastic composites (WPC) [\[135\]](#page-65-0), [\[136\]](#page-65-1). Other options are the conversion of digestate in a solid fuel (pellets) [\[137\]](#page-65-2), or its integration in thermochemical processes as pyrolysis, gasification, and hydrothermal carbonization [\[138\]](#page-65-3).

Figure 18: Scheme of the circular economy of the organic waste, using anaerobic digestion process.

5.2 Pyrolysis as an alternative for the conversion of the solid part of the digestate

All the mentioned alternatives represent a way to re-integrate the digestate to the productivity chain, other than waste it in a landfill or be left in the environment. However, Twence B.V. has recently taken over a pyrolysis plant, and the integration of the anaerobic digestion process and the pyrolysis process can add some synergy for the company business. Therefore, this technology was selected to be compared with the ethanol production process presented in previous chapters.

Pyrolysis is defined as the thermal decomposition of materials at elevated temperatures, that can vary from 350 °C to 800 °C depending on the residence time of the particles [\[139\]](#page-65-4), in an inert atmosphere [\[140\]](#page-65-5). Figure [19](#page-49-0) presents a scheme of the pyrolysis process and some of the products that it can produce. Initially, the feedstock should be dry, and in a small size, the reactor will provoke the thermal decomposition of the material in smaller molecules due to high temperatures. The solid and the gas parts of the stream resulting from this decomposition is directed to a separator where the solids leave the system as pyrochar or biochar. The condenseble gases form the bio-oil [\[126\]](#page-64-7).

Figure 19: General scheme of the pyrolysis process.

Pyrochar can be used as a soil amendment because it is rich in carbon and can stay in the soil for many years. Some studies show benefits for the soil fertility of acidic soils, increasing agricultural productivity and protection against some foliar diseases [\[123\]](#page-64-4), [\[124\]](#page-64-5). From pyrochar, it is possible to produce activated carbon, which is a material with high porosity, with the capacity to selectively collect gases, liquids or impurities inside, because of its high surface area. It has various applications such as air purification, water purification, sewage treatment, metal extraction and can be used for gas storage, among other applications. The process to obtain activated carbon initiates from the production of pyrochar and follows with the activation using $H₂O₂$ or KOH [\[125\]](#page-64-6).

Bio-oil, also known as pyrolysis oil, is being investigated as a future substitute for petroleum. The uses of bio-oil are under different level of development. Applications include the production of heat and power, automotive fuels and biorefineries, however only heat and power commercial-scale demonstrated. Finally, the gas stream is a mixture of gases containing mainly hydrogen and carbon monoxide, diluted in nitrogen; it can be used to create synthetic natural gas (SNG), ammonia or methanol [\[126\]](#page-64-7).

Some alternatives to integrate anaerobic digestion and pyrolysis can be found in the literature. Monlau et al., 2016 [\[127\]](#page-64-8) made a comparison between solid-digestate and the pyrochar from solid-digestate as a soil amendment and the results showed that the content of P and K are richer, as well as the heavy metals concentration, in pyrochar, while the N content keept the same proportion. Also, they verified that pyrochar exhibited a higher surface area and water holding capacity.

Hübner et al., 2015 [\[128\]](#page-64-9) tested the anaerobic digestion of aqueous pyrolysis liquor derived from pyrolysis of solid digestate and reached considerable biogas production for low concentration of the pyrolysis liquor, due to the breakdown of lignin structure. Salman et al., 2017 [\[129\]](#page-64-10) also tried to integrated anaerobic digestion and pyrolysis, but using biochar from pyrolysis of the digestate as a feedstock for the anaerobic digestion process. The results showed an increase of about 20% of the biomethane volume produced. Wei et al.,2018 [\[130\]](#page-64-11) conducted the pyrolysis of the digestate for phenol production because of the high lignin content of the solid digestate.

5.3 Comparison between ethanol production and pyrolysis of the solid part of the digestate

Comparing both methods to obtain products from the solid part of the digestate, the biochemical process to produce ethanol is a cost and energy-intensive process that produces a commodity that is quickly sold in the market. However, the production of lignocellulosic ethanol is facing some problems with many industrial plants closing or having difficulties to be competitive with first-generation ethanol or with oil derivates. The pyrolysis process is also costly and energy-intensive, but more simple than ethanol production, taking into consideration the number of processes. It does not produce a commodity, which can bring difficulties to sell as product, but also the integration of pyrolysis and anaerobic digestion can bring some increase in the biogas production of the anaerobic digestion process.

Nevertheless, a further analysis of the pyrolysis of SPD would be required to draw some conclusions on the feasibility of the process.

6 Conclusions

In the present work, the production of ethanol from the solid part of the digestate from cattle manure was evaluated, through process simulation and literature research, to verify the feasibility of it for Twence B.V.. The primary motivation to develop second-generation ethanol is to avoid the use of the feedstock that compete with the production of food, as it is done with first-generation ethanol; but also, to have a renewable fuel to feed our transportation.

The feedstock to this production comes from the anaerobic digestion process of the cattle manure and after the solid-liquid separation. The design of this process took into account the biochemical route to convert biomass into fuel. The selection of the pretreatment between dilute acid and dilute alkali processes was discussed. According to literature research the dilute alkali process, using sodium hydroxide, recovers more cellulose and hemicellulose, than the dilute acid one. Moreover the yields of glucose from the enzymatic hydrolysis of the pretreated stream were also higher, probably due to the alkali nature of the feedstock.

During the analysis of the feedstock composition, it was realized that the relatively high content of nitrogen could decrease the availability of sugars due to the temperature above 140°C Maillard reactions and the contents of calcium could inhibit the enzymes work. Then, during the process design, the conditions of the pretreatment were kept mild, and a washing step of the fibers with a low pH stream was designed to wash out the calcium content and also the sodium hydroxide.

The hydrolysis of the fibers was done by enzymes in separate reactors from the fermentation process. After a separation process, ethanol was concentrated using a molecular sieve to produce anhydrous ethanol. Which has higher price and fuel grade than the azeotrope mixture of ethanol and water. The non-used part of the biomass was directed to an evaporator and after that feeded to a steam generator that generates steam and power to the system.

After that, an economic analysis of the designed system was done. For that, equipment sizing and cost evaluation of the pieces of equipment were done. Two scenarios were defined; first, a grass-root scenario considered that all the facilities needed to be built from scratch, and in the other scenario, called optimistic, the utilities, such as electricity, steam, and related equipments and wastewater treatment were provided by the facilities that already exist in Twence B.V.

Both scenarios presented production costs higher than the sales, even when governmental subsidies are considered. In the first scenario, the sales come from ethanol production and electricity and district heating production. In the second scenario the revenues come from the farmers that pay to the company to treat for the digestate and from ethanol.

When comparing with other studies, it was possible to verify that the reasons for the revenue from ethanol being insufficient to cover the costs of the plant are: the content of carbohydrates in the feedstock is lower than for other feedstocks, for instance, agriculture residues; the loss of carbohydrates during the pretreatment and the solid-liquid separation after that affect the ethanol production sensibly, and the similar studies of techno-economic analysis of lignocellulosic ethanol, these losses are not counted.

Most of the studies defined a minimum ethanol selling price based on a cash flow analysis. However due to the fact that the sales are lower than the cost a cash flow analysis was not done in this project. However, considering the price that the ethanol needs to be sold to the sales have the same value of the costs, it was possible to verify that in general the biorefineries searched are designed for higher flows of dry matter than this project.

Finally, a comparative study on other alternatives to integrate the solid part of the digestate into the circular economy was discussed. As Twence B.V. has already pyrolysis facilities some suggestions to integrate anaerobic digestion process with pyrolysis was investigated, researches claim that the pyrolysis oil of the digestate can be further digested and increase the biogas production in about 20%; however, the technology needs to be further investigated to verify its feasibility.

7 Recommendations

As the project proved to be more costly than the possible revenues that it can generate, some recommendations are needed for possible future works.

- Small-scale experiments would help to verify if the assumptions used in this work are valid for the feedstock available in this region. Further analysis needs to be done to verify if the composition used in this model is in accordance with the composition of the solid part of the digestate for this region in the Netherlands. And also, if the conversion rates of carbohydrates to sugars and sugars to ethanol are valid, the same can be said to the losses of carbohydrates in the pretreatment.

- Solid part of the digestate has a low content of carbohydrates and high content of lignin, ashes, and extractives when comparing with other feedstocks. Therefore, a mixture of the SPD with a high content carbohydrate waste stream is suggested. Paper sludge is a high content cellulose waste stream; the problem with that is the high content of fillers, like calcium carbonate. However, these can be integrated into the design project, since it also deals with the content of calcium carbonate in the solid part of the digestate.

- As the costs of sodium hydroxide are quite high, an analysis with dilute acid as pretreatment could be further investigated the feasibility of to use another pretreatment.

- Other studies, which achieved a minimum selling ethanol price compatible with the market ethanol selling price, are from ethanol plants designed to handle higher streams. One recommendation is to increase the capacity of the plant to verify the effects of scale economy. However, it needs to be take into account how much feedstock is available in the region for such large operation.

- Alternatives to second-generation ethanol plant need to be further investigated. In this project pyrolysis was mentioned, but other processes, such as gasification or either recovery of chemicals, need some attention.

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Appendix A - Lang factor breakdown

Lang factor breakdown.

Appendix B - CE index

Appendix C - Efficiency equations

Efficiency calculations

A comparison with other studies was made taking in consideration the study made by [\[108\]](#page-63-1). Equation [1](#page-68-0) defines the biomass-to-fuel thermal efficiency, where the numerator is the total energy inside the produced ethanol \dot{Q}_{fuel} and the denominator is the total energy available in the original biomass $\dot{Q}_{feedback}$, the values considered in this evaluation.

$$
\eta_{btf} = \dot{Q}_{fuel} / \dot{Q}_{biomass} \tag{1}
$$

Equation [2,](#page-68-1) defines the thermodynamic efficiency of the system, η_{th} as the ratio between the total energy obtained in the fuel, \dot{Q}_{fuel} , plus the exceeding electricity produced by the system, \dot{P}_{el} , and, plus the exceeding heat produced by the system, \dot{Q}_{ex} , divided by the total energy available in the original biomass $\dot{Q}_{feedslock}$.

$$
\eta_{th} = (\dot{Q}_{fuel} * \dot{P}_{el} * \dot{Q}_{fuel}) / \dot{Q}_{biomass}
$$
\n
$$
(2)
$$

Appendix D - Mass balance of the system

* For the optimistic version the stream of the fuel that goes to Twence and the stream that goes to the wastewater treatment in Twence are S-605 and S-701, respectively. Streams from S-606 to S-621 and streams from S-703 to S-710 do not exist.

* For the optimistic version the stream of the fuel that goes to Twence and the stream that goes to the wastewater treatment in Twence are S-605 and S-701, respectively. Streams from S-606 to S-621 and streams from S-703 to S-710 do not exist.

Appendix E - Equipment sizing and cost evaluation Appendix E - Equipment sizing and cost evaluation Equipmente sizing and cost evaluation per type of equipment, correlation from Seider et al., 2010 [85]. Equipmente sizing and cost evaluation per type of equipment, correlation from Seider et al., 2010 [\[85\]](#page-62-0).

Compressor

Distillator

Evaporator

Heat exchanger Heat exchanger

Pretreatment reactor Pretreatment reactor

Pumps

Six-tenths factor Six-tenths factor

Calculations based on six-tenths factor correlation [85]. Based values from $[107]$ and $[78]$. Calculations based on six-tenths factor correlation [\[85\]](#page-62-0). Based values from [\[107\]](#page-63-0) and [\[78\]](#page-61-0).

Solid handling

Solid/liquid separator Solid/liquid separator

Steam generator Steam generator

Turbine/Generator Turbine/Generator

Wastewater treatment Wastewater treatment

Equipment cost evaluation per area of the process, [85]. Equipment cost evaluation per area of the process, [\[85\]](#page-62-0).

Area 100 - Front-end operations Area 100 - Front-end operations

Area 200 - Pretreatment Area 200 - Pretreatment

Area 400 - Fermentation Area 400 - Fermentation

Area 500 - Separation and purification Area 500 - Separation and purification

Area 600 - Evaporator, boiler and turbogenerator Area 600 - Evaporator, boiler and turbogenerator

Area 700 - Wastewater treatment Area 700 - Wastewater treatment

Appendix F - Utilities consumption and production

Electricity consumption/production

Steam consumption/production

Cooling and chilled water consumption

