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Overall process analysis for on-farm production of bioethanol and protein from leguminous crops

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Aalto University
School of Engineering
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Overall process analysis for on-farm production of bioethanol and protein from leguminous crops

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Technology

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ABSTRACT OF THE MASTER'S THESIS

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One of the main challenges the current world must face is feeding its population. Focusing on the European Union, one of the commodities that suffer from a significant imbalance between local/regional production and consumption is high-protein crops, such as legumes. The advantages of decreasing import dependency are obvious, but a successful commercial production of selected high-value components from grain legumes - i.e. protein concentrate for direct food or feed use - will only be possible along with the exploitation of all fractions of the plant. At this point, the term “biorefinery” appears. “Peas on Earth” is a concept that aims to enhance the yield of feasible product outputs from leguminous crops, offering an opportunity for European farmers to make legumes more available as part of their crop rotation. The outputs of the proposed biorefinery are protein concentrate, sugar (and/or bioethanol) and biomass briquettes. In order to commercialize this technology, detailed calculations on product mass balance, energy use of the biorefinery and heat integration opportunities are required. The objective of this work was, therefore, to supply all this information. This was performed by describing, building and using a simulation model on Aspen Plus that calculates mass and energy balances of the overall process. Pinch analysis was chosen as the methodology for heat integration purposes. The results of the simulations provided the annual production of the plant and a considerably realistic basis for energy demand estimation and for gross profit calculations. The heat integration analysis indicated potential heat savings by transferring heat between specific process streams.

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SAMMANFATTNING AV EXAMENSARBETET

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En av de största utmaningarna som dagens värld möter är att föda sin befolkning. En av de råvaror i Europa som påvisar en betydande obalans mellan lokal/regional produktion och konsumtion är proteingrödor, som t.ex. baljväxter eller trindsäd. Fördelarna med ett minskat importberoende är uppenbara. Dock är kommersiell produktion av utvalda högvärdeskomponenter från trindsäd - dvs. proteinkoncentrat för direkt livsmedel eller foder - endast möjligt om alla fraktioner av växten utnyttjas. Det är i ett sådant sammanhang som begreppet “bioraffinaderi" blir relevant. "Peas on Earth" är ett projekt och koncept som syftar till att öka utbytet av produkter från baljväxter och att erbjuda möjligheter till EU:s jordbrukare för att göra baljväxter mer tillgängliga som en del av växtföljden. Produkterna från bioraffinaderiet är proteinkoncentrat, socker (och/eller bioetanol) och cellulosabriketter. För att kommersialisera denna teknik krävs detaljerade beräkningar på produkters uteffekt, energianvändning av bioraffinaderiet och möjlighet till värmeväxlings integration. Syftet med detta arbete var därför att tillhandahålla denna information. Detta utfördes genom att beskriva och bygga en simuleringsmodell på Aspen Plus. Simuleringsmodellen beräknar material- och energibalanser i de olika processdelarna. ”Pinch”-analys valdes som metod för värmeintegrationsändamål. Resultaten av simuleringarna förutsatt anläggningens årsproduktion och en betydlig realistisk grund för uppskattningen av energiefterfrågan och för bruttovinstberäkningar. Värmeintegrations analys visade potentiell värme besparing genom att överföra värme mellan processflöden.

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Preface

The work for this thesis is a contribution to the Peas on Earth concept carried out under the auspices of the Swedish company Renetech AB. Renetech AB is focused on project development in the areas of renewable energy as well as nutrient recycling in agriculture from biomass. In this project, Renetech collaborates with Ecoetanol AB, a Swedish company that aims at implementing a patented process for processing field beans for food, feed and various fuels, which indirectly also justifies the increased cultivation of this nitrogen-fixing crop. This report is my final thesis for the Master of Science degree at Aalto University in Finland, as a part of a Double-Degree programme shared with KTH Royal Institute of Technology in Sweden. The instructor for this work David Bauner, CTO of Renetech, is warmly thanked for the coordination, help and fruitful discussions, as well as the president of Renetech, Tom Walsh. I would also like to thank them for valuable experience and friendly atmosphere. Prof. Mika Järvinen and Dr. Loay Saeed are gratefully acknowledged for the supervision and feedback on the final report. Finally, I would like to thank the whole group of partners in the Peas on Earth project for their willingness to help me in any question that appeared during the execution of this thesis.

Stockholm, December 2014.

Abbreviations and Acronyms

CFuge	Centrifuge filter
CO_2	Carbon dioxide
C5	Pentose
C6	Hexose
DM	Dry matter
DSTWU	Model for Shortcut distillation design on Aspen Plus
EU	European Union
HEN	Heat exchanger network
HMF	Hydroxymethyl furfural
H_2O	Water
IG	Ideal Gas
mCp	Specific heat capacity flow rate
mCp_{Cj}	Specific heat capacity flow rate of a cold stream in the analysis
mCp_{Hi}	Specific heat capacity flow rate of a hot stream in the analysis
MER	Maximum Energy Recovery
MW	Molecular weight
N	Number of process streams & utility types above & below pinch
n_C	Number of cold process streams present at the Pinch points
n_H	Number of hot process streams present at the Pinch points
NREL	U.S. National Renewable Energy Laboratory
NRTL	Non-random two-liquid activity coefficient model
O_2	Oxygen
PDS	Product design specification
PoE	Peas on Earth
ProtSol	Dissolved protein
RadFrac	Model for Rigorous distillation design on Aspen Plus
RKS	Redlich-Kwong-Soave equation
RStoic	Stoichiometric reactor
Solunkn	Unknown soluble solids
TCBB	Ireland’s national Technology Center for Biorefining and Bioenergy
T_{pinch}	Pinch temperature
$T_{pinch\ cold}$	Pinch temperature for cold streams
$T_{pinch\ hot}$	Pinch temperature for hot streams
$U_{min,MER}$	Minimum number of units in MER network
UNIFAC	Universal functional activity coefficient model
UNIQUAC	Universal quasi-chemical model
VLE	Vapor-Liquid Equilibrium
ΔT_{min}	Minimum allowed temperature difference in heat exchangers
h	hour
kg	kilogram
kWh	Kilowatt hour
L	Litre
SEK	Swedish crown

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Chapter 1

Introduction

1.1 Background on Legumes as Feedstock for Protein Concentrate & Biofuel

One of the main challenges the current world must face is feeding its population, a population that is steadily increasing in size and wealth (Godfray et al., 2010). Apart from the increase in number of inhabitants on the Earth, the increased wealth of part of this population exacerbates this challenge, as wealthy populations tend to demand more meat in their diets (McMichael et al., 2007). In terms of protein content and energy use, animal feed requirements are much higher than actual human requirements when accounting for the daily maintenance of the animals (Dale et al., 2009). As a consequence, it is clear that one of the main challenges for food security is providing enough animal feed, rather than direct human consumption. Although animal nutrition is complex and demands several nutritional requirements, the two dominant requirements are caloric intake and protein (Ensminger & Olentine, 1978). The latter component, protein, is the focus of this thesis.

Although all food plants provide protein, the seeds of the plants that belong to the legume family (*Fabaceae*) are especially rich in protein. The so-called *protein crops* are therefore legumes and include those generally used for their seeds, i.e. grain legumes (also known as *pulses* in some countries), e.g. species like faba bean, pea, chickpea, lupins and soya bean (European Union, Committee on Agriculture and Rural Development, 2013). In general terms, the production of protein crops within the European Union has followed a decreasing tendency during the last decades. Protein crops are now grown on only 1.8% of arable land in the EU compared with 4.7% in 1961, this probably due to the comparative yield advantage of cereals over protein crops grown in Europe in part due to challenges in legume cultivation. However, European consumption of plant protein on a per capita basis is amongst the highest in the world. As a result of this imbalance, the EU now imports 70% of its requirement for high-protein crop commodity, which in 2011 accounted for about 14% of the world-wide production of soya bean. This figure means that imports of protein crop require circa 15 Mha of arable land outside the EU (European Union, Committee on Agriculture and Rural Development, 2013).

Soya bean meal and rapeseed cake are the main types of imported protein concentrate used to enrich the cereal-based feeds produced in the EU (Dahlström et al., 2011). This phenomenon leads to a strong dependence of the EU on imported protein crop commodities and, not less important, a significant environmental impact due to both transport and land use in the producer land, e.g. some studies have shown that soya beans represent a powerful threat to tropical biodiversity in Brazil (Fearnside, 2011). Lifecycle assessments have evidenced that replacing imported soya bean with European-grown protein crops would considerably reduce the resource use and environmental impacts of livestock products (European Union, Committee on Agriculture and Rural Development, 2013).

It is therefore interesting to find alternatives for protein production within the EU that lead to lower environmental impact. According to a study published by the European Parliament in 2013 called “The environmental role of protein crops in the new common agricultural policy”, recent changes in some of the economic drivers behind protein crop production may give incentives to their cultivation. The reasons for it are the following: protein crop prices have in recent years increased slightly faster than wheat prices, imported soya feed has become more costly, and fertiliser prices are also increasing significantly. As a result, the competitive position of legumes produced in the EU has improved in the last decade (European Union, Committee on Agriculture and Rural Development, 2013), and this provides a new opportunity for enhancing this alternative.

In order to get a complete view on the possibilities to increase the grown protein crops in the EU, another advantage of these crops must be also highlighted. Not only are legumes interesting due to their high content in protein, but also almost all of them perform biological nitrogen fixation. This functional property is unique among crops, and the legume plant supplies the soil with nitrogen and therefore reduces the need for fertiliser nitrogen in the following crops (European Union, Committee on Agriculture and Rural Development, 2013). Thus, legumes can play a critical role in crop rotation, by reducing fertilizer (and thus energy) costs, improving soil physical conditions and decreasing pest and weed populations (Jensen et al., 2010). In fact, several studies have been done on the capacity of legumes for climate change mitigation (see the review article by Jensen et al., 2010).

Eventually, an increase in demand for grain legumes and the aforementioned improvement in their competitive position may increase the attractiveness of this commodity to European producers as a rotation crop. However, if European protein crop production is to compete better with the more profitable European cereals production, a successful commercial production of selected high-value components from grain legumes (i.e. protein isolate or concentrate for direct food or feed use) will require the exploitation of all fractions of the plant, in order to maximize plant biomass valorization and minimize the production of residues. At this point, the concept of "biorefinery" appears. According to Cherubini (2010), the fundamental aim of a biorefinery is "to deliver multiple products by polymerising and deoxygenating the feedstock components, thereby maximising the value derived for the biomass feedstock". One of these multiple outpus is very commonly a biofuel, e.g. biogas, bioethanol, or biomass briquettes. Indeed, grain legumes are very interesting as a substrate for biorefineries, particularly because leguminous plants are not dependent on nitrogen fertilisation. Their capacity to fix nitrogen leads to lower fossil energy use, which in turn leads to a lower carbon footprint (Karlsson et al., 2014).

If the biorefinery concept is brought into consideration for the legumes case, the agricultural sector in charge of growing protein crops can be re-created to support both increased feed needs and biofuels production.

Like that, the two challenges mentioned at the beginning of this text may be tackled simultaneously, i.e. the high protein content and energy use in animal feed requirements, which in turn is continuously increasing due to wealthier populations in some parts of the world. Accordingly, crops such as faba beans (*Vicia faba L.*), which contain significant amounts of both protein and starch, are seen as an agronomically viable alternative. Yet for the protein concentrate production from faba beans to be economically feasible, all the possible by-products need to be made profitable.

Many studies have already been performed on the ability to separate protein from starch in beans, and it has been shown that bean starch is readily convertible to ethanol using the same process and enzymes applied to corn - see for example Nichols et al. (2011). Consequently, on-farm production of bioethanol from the starch contained in legumes after protein separation is an attractive option for a biorefinery proposal, together with the exploitation of other possible by-products. Among these we find the explotation of the lignocellulosic fraction of the leguminous plant. Lignocellulose refers to agricultural residues such as rice straw, wheat straw, corn stover, bagasse, and plant residues in general (Tojo & Hirasawa, 2013). This type of biomass may be processed to produce biomass briquettes or pellets for self-heating purposes, or to produce lignocellulose-derived ethanol that would increase the biofuel yield of the biorefinery.

1.2 Peas on Earth Project

The company Ecoetanol AB, based in Sweden, has developed a technology concept where ensilaged pea or bean plants are decomposed into three fractions: protein-rich liquid extract, beans and stalks. This concept is called Peas on Earth (PoE).

This separation is done by means of processing the whole plant above ground by first ensilaging it, and then passing the ensilaged biomass through a wet thresher earlier developed by Ecoetanol. The objective of the PoE concept is that the three fractions are further processed into a variety of products. Therefore, the concept as a whole can be referred to as a biorefinery. The products considered as possible outputs of this biorefinery concept are: protein concentrate, sugar (dextrose), briquettes, bioethanol, and fertiliser. In order to produce these commodities, one of the crucial steps in the biomass processing is the separation of the protein content from the starch content of the bean or pea grains.

According to Ecoetanol, by enhancing the yield of the feasible product outputs from leguminous crops, the PoE technology appears as a clear opportunity for European farmers to make legumes more accessible as part of crop rotation; this by simultaneously increasing the amount of organic matter in the soil and reducing the need for mineral fertilizer, while offering additional income from the products mentioned above.

The partners taking part in the concept's development are Ecoetanol AB, Renetech AB (both based in Sweden), the Technology Center for Biorefining and Bioenergy (TCBB, based in Ireland), and Industrias Agrarias Castellanas S.A. (based in Spain).

1.3 Goal of the Study

This thesis has been performed in collaboration with Renetech AB, which has engaged in managing market aspects and industry permits for commercialization of the PoE technology. Moreover, Renetech works with the development of the system aspect of the PoE technology, and with the project management required to develope a Demonstrator, i.e. a pilot plant of the future commercial biorefinery. For all these reasons, Renetech is interested in obtaining detailed calculations on the product mass outputs, energy use of the plant, and opportunitites for heat integration, according to a given input of leguminous biomass with a characteristic composition.

The aim of the thesis was therefore to provide Renetech with this desired information. This was performed by describing, building and using a simulation model that calculates mass and energy balances of the overall process. The process converts the three fractions obtained from the ensilaged legumes into a variety of products, such as bioethanol, protein for feed/food grades and, eventually, other by-products interesting for sales. The model should provide an easy-to-use, yet rigorous, tool for evaluation of the mass and energy balances. Opportunities for heat integration in the process should also be identified.

The target group for the study was Renetech and, secondly, the rest of the partners in the PoE project. Results should be useful as information for economic evaluations, but also for comparison of the environmental performance of the products from the present biorefinery with conventional products.

It must be highlighted that the product mass outputs and economic assessment included in this work was considered as sensitive information that all partners in the PoE concept's development would like to keep confidential. Therefore, due to the Non-Disclosure Agreement signed with Renetech AB, two versions of the thesis report have been elaborated. Only the classified report that is delivered to the company contains this confidential data.

1.4 Thesis Layout

This thesis includes eight chapters. Chapter 1 introduces the motivations and the objectives in developing this study. Chapter 2 shows an overview of the most relevant information obtained from literature review during the earlier steps of the study. Chapter 3 reviews step-by-step the approach to build the foundations required before developing the simulation models. Chapter 4 gives a description of the built models in the simulation software. Chapter 5 describes in detail the heat integration analysis executed on two of the Process designs. Chapter 6 covers the scheme followed to do the economic assessment. Chapter 7 is the discussion of the results and incorporates some recommendations for future work. Finally, Chapter 8 presents the conclusions of this work.

Chapter 2

Literature Review on the Production of Protein Concentrate, Dextrose, Briquettes and Ethanol

A literature review gives an overview of the field of inquiry. In this case, the goal of the literature review was to get familiar with the essential background on the production process of each of the possible outputs of the biorefinery. This step was crucial in order to later build the foundations for the simulation model and, thus, to build the model itself.

2.1 Protein-Starch Separation in Bean fraction

Researchers have tried different methods to separate starch and protein from legumes and improve starch and protein purification. But the isolation of starch fraction from legume seeds is difficult to achieve due to the presence of insoluble flocculent proteins and fine fibre which diminishes sedimentation, as these fractions co-settle with the starch fraction (Emami et al., 2007).

Most of the literature found regarding commercial separation of protein and starch concerned corn fractionation, which mainly uses the wet milling process. In this process, the grains are steeped in sulphur dioxide and lactic acid followed by a grinding step. The starch and protein are then separated using settling, centrifugation or hydrocycloning (Lindeboom, 2005). All of these processes are based on the difference in density between the starch and the hydrated protein particles. Thus, sedimentation is a proper technique to separate these two components.

In general, the separation of starch and protein often consists of the solubilisation of the protein (called as protein extraction) and the sedimentation of starch granules out of a slurry. For the beans case, the bean seeds first need to be milled to flour. Pin-milling of bean seeds, either whole or dehulled seeds, yields thus flours that contain two distinct types of particles based on both their size and density. This distinction can be exploited to produce a protein concentrate (the light population of particles) and a starch-riched slurry (the heavy population of particles) (Vose et al., 1976).

Starch sedimentation occurs due to the average density of starch granules (1.5 g/cm3), which is greater than that of the protein particles (1.1 g/cm3) (Lindeboom, 2005). The rate of this phenomenon could be determined by Stokes' law, which proves the relationship between particle density and sedimentation.

2.2 Production of Protein Concentrate

As described for the starch-protein separation process, protein is generally recovered from the feedstock by extraction with a suitable solvent (usually aqueous) with the aim of producing an enriched protein product. Depending on the type of proteins present in the feedstock, the protein is best extracted in water, aqueous salt solution, 70-80% ethanol or alkali/acid. The result of protein extraction is an intermediate that is much diluted with the extraction medium. Therefore, the next step in protein production is concentration (Lindeboom, 2005).

In the case for this study, the extracted protein from the beans fraction is mixed with the juice extract, i.e. one of the three outputs from the wet thresher. The protein in the juice extract can be concentrated through a variety of methods, however, the most common method is heat coagulation (Bals et al., 2012). This unit operation is required because the protein particles will not sediment with conventional physical methods (e.g. filtration or settling) unless they are first agglomerated through coagulation. What occurs during coagulation is that proteins are denatured due to high temperature, thus hydrophobic sites are open up and this causes the proteins to coagulate and precipitate. Coagulation can be achieved through heating in a short residence time. The coagulated protein produced is then separated from the de-proteinated juice by filtration. Finally, the filtrated protein is dried (Bals et al., 2012). After this purification process, the extracted proteins are referred to as protein concentrates or protein isolates, depending on the protein purity of the sample.

2.3 Dextrose Production

Dextrose or glucose is an all-purpose sweetener that is used in countless foods, beverages, sweets, and nutraceutical products across the globe (Hobbs, 2009). Dextrose can be produced from starch processing, as starch is formed by long chain molecules built by glucose (i.e. a molecule classified as *hexose*, since it contains 6 carbon atoms).

Acid hydrolysis of starch was the main technique used in the past. However, acid hydrolysis is now largely replaced by enzymatic processes, as the former one required the use of corrosion resistant materials, gave rise to high colour and salt and ash content, needed more energy for heating and was relatively difficult to control (Chaplin & Bucke, 1990).

Today, commercial processes on dextrose production which are based on enzyme-catalysed conversion have mainly three stages. It starts with the starch slurry (30% to 40% dry solids) undergoing the so-called *gelatinisation* step. In this step, the slurry is first pasted at a temperature of 80–90°C, which leads to a phase transition. The gelatinisation process breaks down the intermolecular bonds of starch molecules in the presence of water and heat. This irreversibly dissolves the starch granule, and the heat causes the chains to begin to separate into an amorphous form (Hobbs, 2009). At this point, the starch thickens considerably and would be difficult to process if an enzyme was not added, partially hydrolyzing the starch to lower molecular weight molecules (Borglum, 1980).

In the next step the slurry undergoes *liquefaction*. Various manufacturers use different approaches to starch liquefaction but the principles are the same. Starch is treated with a ‘heat-stable’ enzyme alpha-amylase at the temperature of gelatinisation, i.e. 80-90°C. During liquefaction, the enzyme alpha-amylase attacks the starch polysaccharide randomly, producing maltose (two glucose monomers together) and higher oligomers, according to:

$$\text{starch} + H_2O \xrightarrow{\alpha\text{-amylase}} \text{oligosaccharides}$$

The principal objective for liquefaction is to reduce the viscosity of the gelatinised starch to ease subsequent processing. The resulting solution of this process step is more capable of flowing, i.e. is liquefied (Chaplin & Bucke, 1990).

The last step in the process involves *saccharification* of the liquefied product using a gluco-amylase enzyme. During saccharification, gluco-amylase attacks the non-reducing end of maltose and of higher oligomers, releasing mainly glucose molecules (fermentable sugars), but also maltose molecules (McAloon et al, 2000). Before the enzyme is added, the liquefied product is cooled down to 60°C. The reaction occurring during saccharification is depicted as follows:

$$\text{oligosaccharides/maltose} + H_2O \xrightarrow{\text{gluco-amylase}} \text{glucose/maltose mixture}$$

In order to refine the resulting liquor from saccharification and make a dextrose (glucose) syrup, the fats and protein are removed by filtration. The syrup is then carbon bleached, i.e. it is passed through pulsed beds of activated carbon for clarification and bleaching. After the carbon beds, the liquor is passed through ‘check’ filters designed to remove escaping carbon fines. Next, the syrup is demineralized through anion and cation exchange resins prior to being isomerized. The resulting refined stream is then concentrated to the desired solids level (typically 75 - 85 % solids) and packaged for sale globe (Hobbs, 2009).

2.4 Briquettes Production

Briquettes are squared or round pieces intended for heating, and produced by compression of biomass particles. Fuel briquettes are at least 25 mm in diameter or width, and they usually have a moisture content below 15%.

The basis of regular briquettes production is the lignin plasticitation mechanism. Lignin and cellulose are the two major compounds of biomass. Lignin is a non-crystallized aromatic polymer that, if heated to 200–300°C, starts to be soft, melted and liquefied. Then, if pressure is also applied, lignin will glue cellulose together which solidifies the biomass and make it become briquettes after cooling down. If no lignin is present in the biomass, a binder must be added.

In general, briquetting biomass involves the following steps: crushing, drying (natural or induced) to moisture content of 6 – 14%, densification at 4-60 MPa and 160-280°C, cooling and packing for storage (Zhanbin, 2011).

2.5 Starch-derived Ethanol Production

In order to produce ethanol from the starch fraction of bean seeds, the first part of the process may be described as exactly the same as for the process described in sub-section 2.3, i.e. dextrose production process. Thus, gelatinisation, liquefaction and saccharification are also required to produce ethanol. However, in this case, saccharification can be completed either *before* fermentation or by a continuous saccharification *during* fermentation. If the first of these two methods is used, then the method is essentially the same as for dextrose production, but with an additional step at the end (fermentation). In this case, the syrup obtained after saccharification is diluted with water to 19 wt% (weight percent) solids and cooled to fermentation temperature, i.e. 30°C.

Currently, the most frequently used micro-organism for fermenting bioethanol in the industry is the yeast *Saccharomyces cerevisiae*, which is capable of fermenting hexoses. This organism is added for fermentation, which converts glucose molecules to ethanol and carbon dioxide, CO_2 (Borglum, 1980). The fermentation process continuously generates heat and thus requires cooling to keep the temperature constant and avoid killing the yeast. The product leaving the fermentation process is water containing grain solids and about 10% - 15% ethanol (Kelly, 2007).

2.6 Lignocellulose-derived Ethanol Production

The stalks obtained as plant residue from the separation of grains and the rest of the leguminous crop are classified as lignocellulosic biomass. Lignocellulose is composed of carbohydrate polymers or polysaccharides (cellulose, hemicellulose), and an aromatic polymer (lignin). Ethanol biofuel can also be produced by fermentation of the hexoses and pentoses (sugars with 5 carbon atoms) that are contained in cellulose and hemicellulose chains.

The first step in conversion of lignocellulose to ethanol is size reduction and pretreatment. Since lignocellulosic materials are mostly insoluble in water, the goal of the pretreatment step performed before hydrolysis is to remove the recalcitrance of this feedstock and expose the cellulose fibers to enzymes (Hahn-Hägerdal et al., 2006). Hemicellulose is normally chemically converted in this step, since its amorphous structure allows an easier conversion than cellulose. The resulting monosaccharides from hemicellulose hydrolysis are both hexoses and pentoses. There are four different types of processes for pretreatment of lignocellulosic materials: physical, physico-chemical, chemical and biological processes. The choice of type of pretreatment depends on the type of feedstock used for bioethanol production (Balat, 2011).

The hydrolysis step involves breaking the glycosidic bonds of polysaccharides, which are the pretreated feedstock, into fermentable sugars, i.e. monosaccharides (either hexoses or pentoses depending on the polysaccharide). This is performed by supplying a water molecule to render each broken bond inactive, and this reaction needs a catalyser (Wang, 2008). Depending on the catalyser, the methods for the hydrolysis of lignocellulosic materials can be classified in two groups: chemical hydrolysis and enzymatic hydrolysis. Chemical hydrolysis involves the exposure of biomass to a chemical (predominantly an acid) for a period of time at a specific temperature. However, one of the major disadvantages of chemical hydrolysis is that sugars can be converted to degradation products like tars, besides environmental and corrosion problems due to acid consumption. In order to prevent these problems, enzymes may be used. The enzymatic hydrolysis has also a low utility cost compared to chemical hydrolysis because it is conducted at mild conditions, besides being an environmentally friendly alternative (Balat, 2011).

If focusing on enzymatic hydrolysis, cellulose is hydrolysed by an enzyme called cellulase, which is actually the name given to a group of enzymes that synergistically hydrolyses cellulose. These enzymes are endoglucanases and exoglucanases or cellobiohydrolases (Balat, 2011). Endoglucanases randomly attack cellulose chains breaking them to release oligosaccharides (being it easier with chains in the amorphous regions), and cellobiohydrolases cleave both cellulose chains and oligosaccharides at their ends releasing soluble sugars such as glucose (Hahn-Hägerdal et al., 2006). Also, hemicellulose is broken down by the enzyme xylanase.

The next step is fermentation. In contrast to fermentation for production of starch-derived ethanol, in the present case fermenting pentoses efficiently is as important as fermenting hexoses. Depending on the lignocellulose source, the feed for fermentation process produced in the hydrolysis step will normally consist of the monosaccharides glucose, xylose, arabinose, galactose, mannose, fucose, and rhamnose (Balat, 2011). Fermentation of this mixture of sugars achieves higher ethanol yields by adding specially developed micro-organisms for their fermentation. The *S. Cerevisiae* yeast suggested for the production process of ethanol from starch can only convert the hexoses, and not the pentoses that are found in the hydrolysis product. Therefore, other micro-organisms are required. As an example, the micro-organism *Zymomonas mobilis* efficiently produces bioethanol from the hexose sugars but, as *S. cerevisiae*, not from pentose sugars. However, some researchers have generated a xylose fermenting *Z. mobilis* by introducing a xylose-metabolizing pathway from *Escherichia coli* (Balat, 2011). Thus, this organism can be added for fermentation, which will convert both hexoses and pentoses to ethanol and carbon dioxide.

Actually, conversion of lignocellulose to ethanol by using enzymes may be performed by following different configurations. Firstly, if enzymatic hydrolysis is performed separately from fermentation step is known, the technique is called “Separate hydrolysis and fermentation”. On the other hand, if these two processes are performed in the same vessel, the configuration is called “Simultaneous saccharification and fermentation”, where cellulases and xylanases convert the carbohydrate polymers to fermentable sugars and other micro-organisms convert them to ethanol, everything in the same vessel. This process has an enhanced rate of hydrolysis compared to the “Separate hydrolysis and fermentation” configuration (Balat, 2011).

2.7 Downstream Ethanol Processing Techniques

After fermentation is completed, the resulting solution containing ethanol is considerably diluted with water and contains several impurities. As a consequence, downstream purification and concentration of ethanol is required before it can be sold as biofuel.

As previously stated, a product of fermentation apart from ethanol is CO_2. This compound is sent to a scrubber that recovers the ethanol and other soluble compounds before emitting the CO_2 to the atmosphere (or collecting it in order to sell it commercially to, for example, the soft drinks industry). Additional CO_2 may be removed by heating the stream and passing it through a degasser drum to flash off CO_2 (Kelly, 2007).

At this point, the ethanol solution must be concentrated. The distillation process removes the majority of the remaining water on the solution based on the difference in boiling points of the two major components, i.e. ethanol and water. The system is most commonly comprised of two or three columns for high concentration. Reboilers in the distillation columns are used to heat the ethanol/water mixture to drive the process. The solids and water, called stillage, are removed from the bottom of the first column. The vapour leaving the first column is 40 - 50% ethanol and flows to the second column, i.e. the so-called rectifier column. The rectifier takes the vapour from the first column and the distillation process continues until it is concentrated to 90%-95% ethanol.

Eventually, a third column may be added, the so-called side stripper. This component takes the water out of the bottom of the rectifier and strips out any remaining ethanol in order to recover it (Kelly, 2007).

Finally, the ethanol purity may be further enhanced according to customer requirements. This is done by the process called dehydration. The dehydration process consists of two molecular sieves units that are cycled so one unit is regenerating (after it became saturated with water) while the other is operating. The vapour leaving the last distillation column passes through a bed of beads where the water is adsorbed on the beads and the ethanol vapour passes through. The ethanol vapour is then cooled in a condenser to convert it to liquid for storage (Kelly, 2007).

Chapter 3

Approach and Design Basis – Foundation for Simulation of PoE Technology on Aspen Plus

Due to the variety of possible outputs from the biorefinery depending on the chosen conversions paths, three Process designs for the PoE technology are suggested and simulated as part of this thesis. The designs are chosen on the basis of commercial viability. The description of each Process design is the following:

- **Process design 1:** This case is the simplest one among the three designs. The products obtained in the biorefinery are the following: protein concentrate for feed grades, purified sugar (dextrose) for the food industry, and briquettes for heating. Thus, in this design, the glucose obtained from starch processing is purified and sold as dextrose/sugar, and no bioethanol production is considered.
- **Process design 2:** In this design, bioethanol production is included, which leads to the exclusion of sugar production for sales to the food industry. The products obtained in the biorefinery are the following: protein concentrate for feed grades, bioethanol derived from the starch, and briquettes for heating.
- **Process design 3:** In this design, ethanol production from lignocellulose is integrated. Thus, briquettes are not produced and instead lignocellulosic biomass is used to produce ethanol. The products of this design are protein concentrate and bioethanol derived from starch, cellulose and hemicellulose.

3.1 Methodology

The goal of separating the simulations in three different Process designs is to obtain the information required to perform an analysis on the trade-offs of producing one commodity or another.

Mass balances are a foundation for process design since they determine the quantities of raw materials required and the corresponding products created according to the sales purposes. In order to simulate the processes and obtain the outputs of the potential products for different plant configurations, mass balances are solved for the three process designs by using Aspen Plus® modelling software (Aspen Technology Inc., USA), supported by Excel® when necessary. Aspen Plus is a commercially available software tool that performs as a steady-state chemical process simulator. The user of the model needs to specify the key parameters of each unit operation and of the inlet streams. Also, thermodynamic databases are required which describe the key physical and chemical properties of each chemical component (National Research Council of the National Academies, 2005). Aspen Plus has been frequently used in modeling of biorefineries (Kadam et al., 2000; Nguyen & Saddler, 1991; Sassner et al., 2008; Wingren et al., 2003a; Wingren et al., 2003b; Wingren et al., 2005; Wooley et al., 1999), and this is the reason why it was chosen for the present work.

As for the energy balances, data on heating and cooling requirements within the process are also obtained by Aspen Plus software. The opportunities for heat integration of the processes are later defined by using another simulation software, i.e. the so-called HINT software. HINT® is specialized in heat integration analysis by Pinch technology and was found as suitable for the purposes of this study (see Chapter 6 for more details).

In Chapter 3, a detailed foundation for simulation of PoE technology on Aspen Plus is provided. It must be highlighted, however, that some unit operations (mainly solid-liquid separators) were modelled with data from results and estimates found on the literature or on other commercial technologies. Thus, solids removal and liquid retention in the solid streams is normally fixed, due to lack of own PoE experimental data. The following sub-sections procure the details of the decisions, calculations and assumptions made prior to and during simulation of the three process designs on Aspen Plus.

The flow diagram on Figure 3.1 shows the approach followed in this study in order to reach the proposed objectives, that is, product mass outputs, energy use of the plant and opportunitites for heat integration.

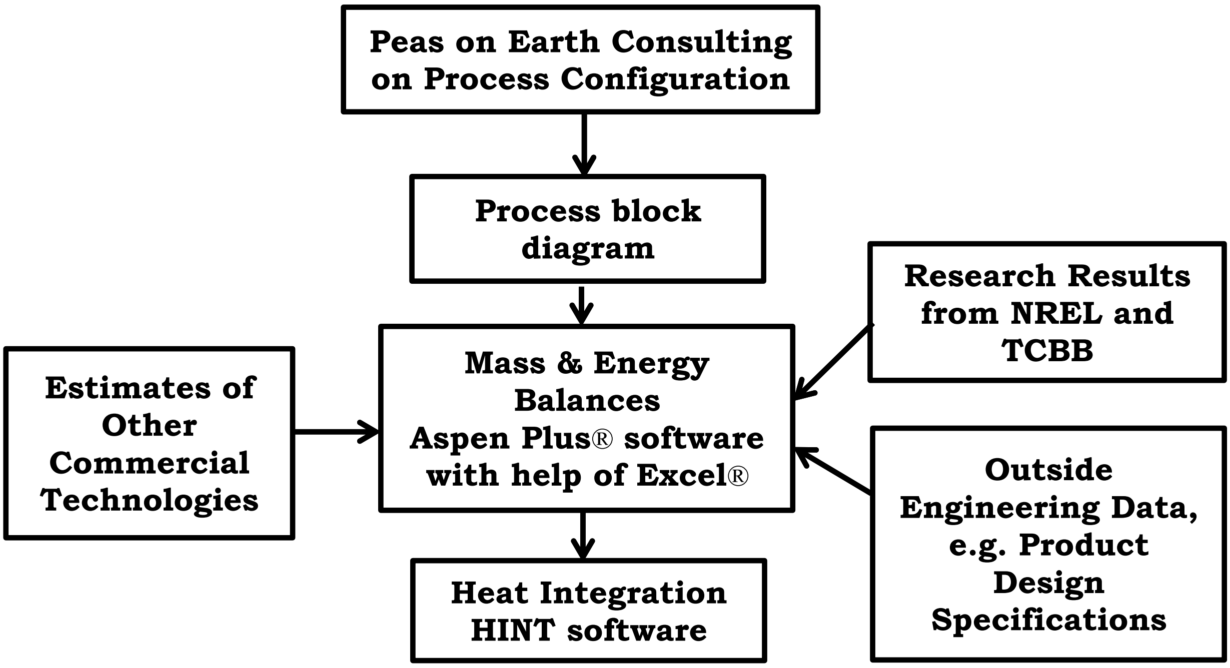

Figure 3.1: Flow diagram for the approach followed in this study

3.2 Block Diagram of the Process

Being Process design 3 the most complex case among the three studied cases, the block diagram of this design (see Figure 3.2) showed to be a very useful tool for understanding the PoE technology in general, prior to simulations on Aspen Plus. Block diagrams often give a comprehensible picture of the process and, thus, the goal of this diagram is to clarify the overall concept without concern for the details of implementation. The principal parts are represented by blocks and their relationships (i.e. mass flows) by arrows. Each block and the whole process for the three Process designs are carefully described throughout the present chapter and Chapter 4.

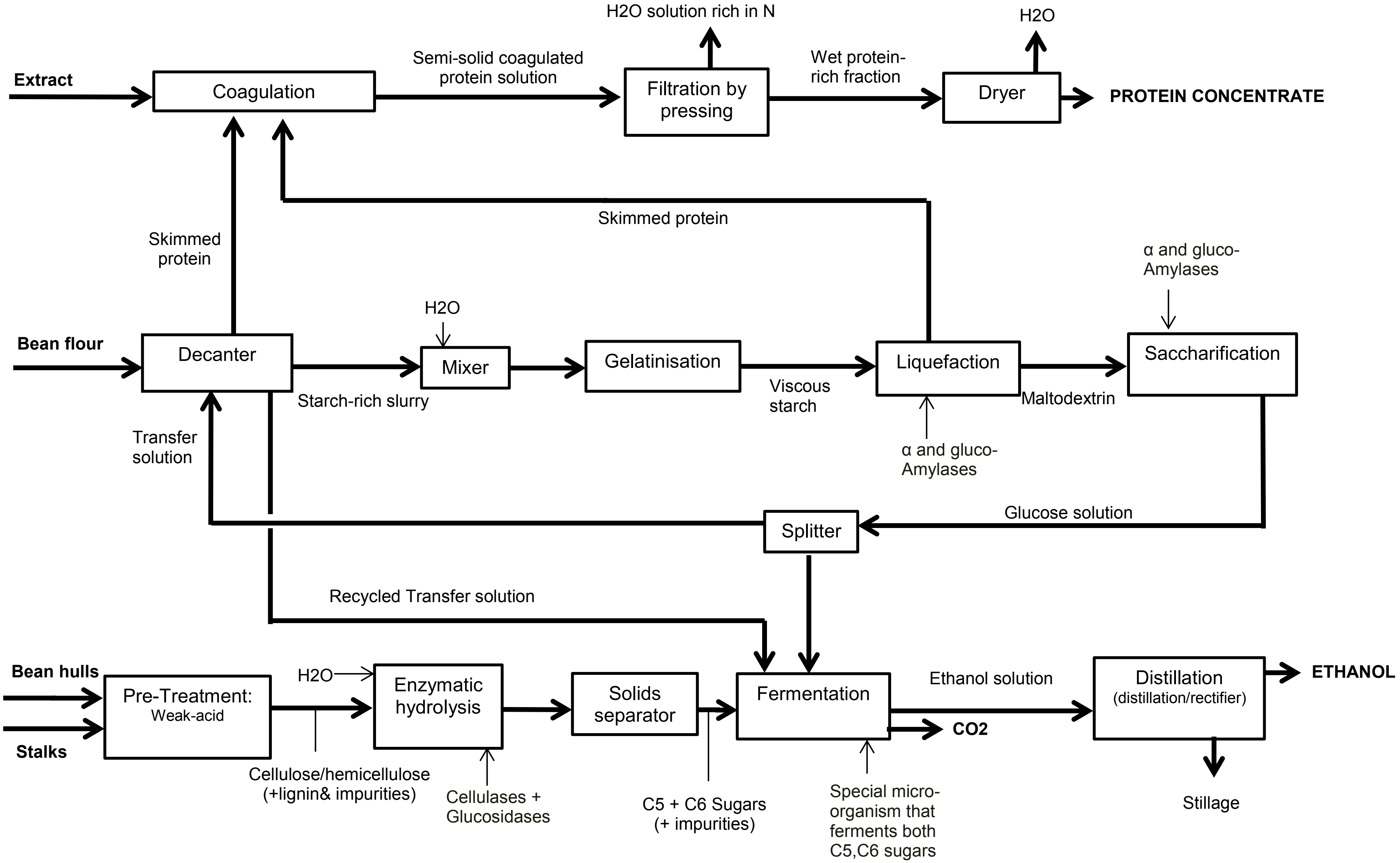

Figure 3.2: Block diagram for Process design 3

3.3 Physical Property Methods

Aspen Plus modelling software requires many parameters and properties of all components present in the simulations. The aim of the collection of parameters and properties prior to simulation is to make the overall designs in the study thermodynamically rigorous and including all the required physical properties. The physical properties were collected from Aspen Plus database and from property data developed by the U.S. National Renewable Energy Laboratory, NREL, specifically for biochemical processes (Wooley & Putsche, 1996).

A property method is a group of methods and models that a simulation software uses to compute thermodynamic and transport properties. Since it is the user who can define the property method, the choice of physical property method is an initial key decision that will determine the accuracy of any simulation results. The most important factors that should be considered when selecting a property method are: the composition of the mixture, the temperature and pressure range, and the availability of parameters (i.e. availability in the simulation software or in literature) (Aspen Plus, 2003). Aspen Plus includes many databanks that contain properties for components as well as binary parameters for different property methods.

In the presented model simulations, high temperature or pressure in the unit operations are not encountered. However, the system becomes highly complex due to the presence of three different phases of matter: solid phase, gas phase, and liquid phase. Consequently, a single physical property method is not sufficient for accurate simulation of this system, and a selection of different methods is done instead.

Aspen Plus offers a guideline for choosing the appropate property methods. This guideline is illustrated in the following diagrams and it was employed for the decision-making process prior to simulations.

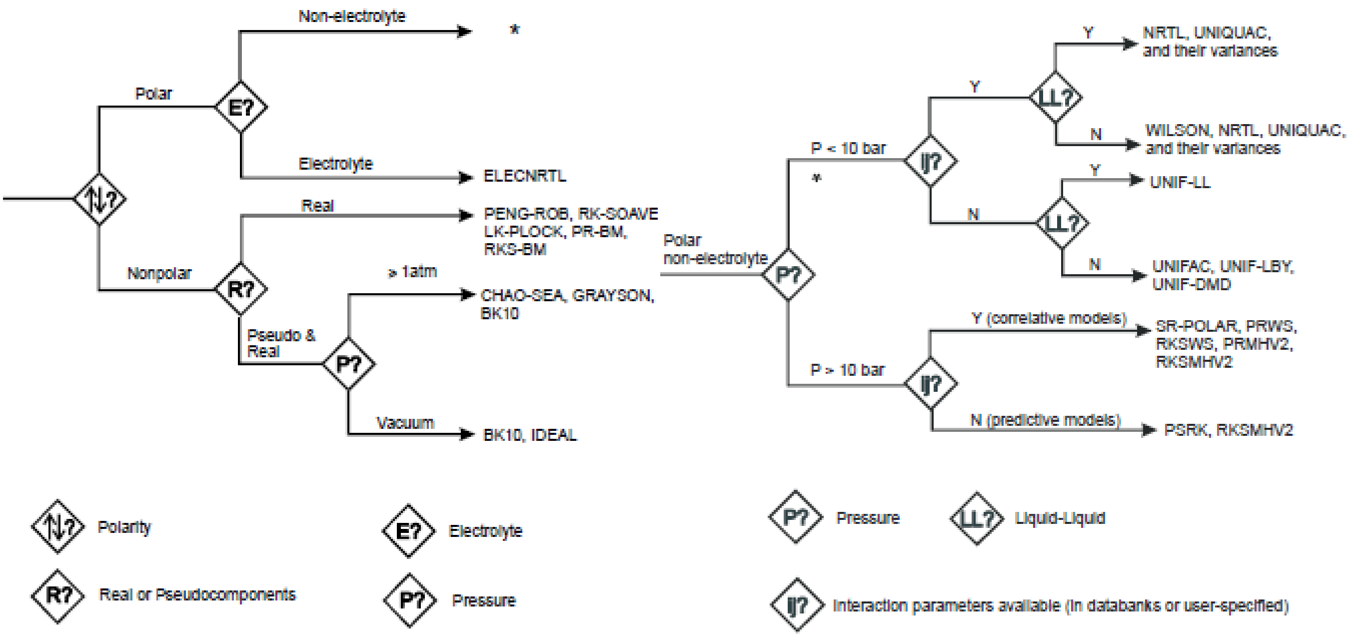

Figure 3.3: Guidelines for choosing a property method (Aspen Plus, 2003)

3.3.1 Global Property Method: Vapor-Liquid Equilibria

First, the global property method has to be defined. The global property method is the default method used by Aspen for all property calculations, unless a different property method is specified for a specific unit operation block or flowsheet section (Aspen Plus, 2003).

According to the guidelines by Aspen Plus, the same path on the diagram in Figure 3.3 is followed for the global property method selection in the three process designs, since all of them involve liquid phase reactions. First, the processes involve polar and non-electrolyte compounds at low pressure. Second, the interaction parameters for vapor-liquid equilibrium of ethanol, water and acetic acid are available on Aspen Plus. And finally, due to the presence of a distillation column, vapor-liquid equilibrium is present, but no liquid-liquid equilibria interaction nor vapor-phase association are expected.

After answering these questions, the guideline diagram leads to a variety of options for activity coefficient methods, such as *non-random two-liquid activity coefficient* model (NRTL), *Wilson* model, *universal quasi-chemical* model (UNIQUAC) and *universal functional activity coefficient* model (UNIFAC). These methods are verified methods and have shown to be successful in predicting Vapor-Liquid Equilibrium (VLE) of non-electrolyte solutions (Wooley et al., 1999). Moreover, these methods are also suggested by Aspen Plus guide (Aspen Plus, 2003) in case of presence of azeotropic separations and/or liquid phase reactions, which are the cases for the studied technology.

According to this, NRTL method is selected as the global property method due to a variety of reasons. The property method NRTL has a wide application for low-pressure ideal and non-ideal chemical systems and it can handle any combination of polar and non-polar compounds, up to very strong non-ideality. Moreover, the standard NRTL model is most commonly used in simulation of ethanol production due to the need to distill ethanol and handle dissolved components (Wooley et al., 1999). On the other hand, the availability of pure-component and binary parameters is a crucial factor for calculating pure-component or mixture properties. Since gathering of experimental data and its regression are not within the scope of this project, the choice of property method becomes highly dependent on the availability of the required parameters on Aspen Plus or on the literature found. Many binary parameters are available for NRTL model in Aspen databases, becoming this another reason for choosing this method.

Finally, the selection of NRTL as the global property method on Aspen Plus includes the NRTL liquid activity coefficient model, Henry's law for the dissolved gases, and RKS (Redlich-Kwong-Soave) equation of state for the vapor phase.

3.3.2 Solubility of CO_2: Henry's Law

The behavior of dissolved gases in the vapor-liquid equilibrium (i.e. CO_2 presence in the distillation column) needs to be computed by an activity-coefficient approach. For Aspen Plus to correctly simulate CO_2, this component is set to be a Henry component, meaning that it is set to obey Henry's law. Aspen Plus has built-in Henry's law parameters for a large number of component pairs (including CO_2), thus the parameters are available.

3.3.3 Solids Definition

Aspen Plus can model solids anywhere in a process flowsheet. A wide range of unit operation models for solids handling equipment is available, e.g. for crushing or grinding. NRTL method is used to calculate properties for components in the liquid and vapor phases, thus another property method needs to be specified for the flowsheet section where solids are processed. In this case the chosen property method is called SOLIDS, which is a property method developed by Aspen Plus for general solids applications (Aspen Plus, 2003).

As a summary, two different physical property methods in Aspen Plus are selected in order to simulate the thermodynamic properties of the components as accurately as possible: standard NRTL method to calculate properties for components in the liquid and vapor phases, and SOLID method to do the respective with solid phases.

3.4 Thermodynamic Parameters and Properties

Thermodynamic parameters and component properties for most of the compounds in the system are obtained from Aspen Plus. However, the property data of the components that are not in the Aspen databank are obtained from the database developed by NREL (Wooley & Putsche, 1996) mentioned in sub-section 3.3, which is specificalized in biochemical processes.

For compounds involved in vapor-liquid equilibrium, the software needs a complete set of properties to allow it to do flash calculations. This applies even to the compounds that have very high boiling points and will stay in the liquid phase exclusively. NRTL uses the Ideal Gas (IG) at 25°C as the standard reference state, thus it requires the heat of formation at these conditions (Aspen Plus, 2003). Table 3.1 presents the minimum required properties that must be provided to the software in case NRTL method is applied.

Table 3.1: Required properties for NRTL method (Aspen Plus, 2003)

Liquids and Gases		**Conventional Solids**
Critical Temperature	IG Heat Capacity	Heat of Formation
Critical Pressure	Heat of Vaporization	Heat Capacity
IG Heat of Formation	Liquid Density	Density
Vapor Pressure		

On the one hand, materials such as glucose and proteins, which are commonly solids but will be used in aqueous solution in a large part of the process, will be treated as liquids in those units. On the other hand, the compounds that are always solids and are identifiable, e.g. starch, ash, cellulose or lignin, are assumed to comprise conventional solids on the simulation software. The advantage of conventional solids on Aspen Plus is that property requirements are very minimal, because they do not need to be described by attributes but by a chemical formula instead (Aspen Plus, 2003). For the polymeric compounds, e.g. cellulose or starch, a chemical formula corresponding to a single repeat unit is used.

The databanks VLE and HENRY on the software were developed by AspenTech using binary vapour-liquid equilibrium data from the Dortmund databank (DDBST Dortmund Data Bank Software & Separation Technology GmbH). In addition to the parameter values, the databanks in Aspen contain temperature, pressure, and composition limits of the data as well as average and maximum deviations (der Merwe & Blignault, 2010). Therefore, for these databank parameters, it is assumed that Aspen can simulate the binary vapour-liquid systems involved in this study and data regression analyses are not done.

Appendix A includes tables with the specification of all the components used from NREL databank, as well as the respective assumptions, properties and parameteres used.

3.5 Plant Location, Size and Operation Parameters

For this project, plant location in terms of geographical area is not specified, although the first plant of PoE project is intended to be built in Sweden. When choosing the plant location, proximity to a sufficient supply of fuel for thermal energy must be considered. The flexibility to utilize more than one source of energy may also be advantageous. Furthermore, the facility also requires adequate electricity and water supply. As for cooling water, it is assumed that the well water is available at the same temperature year round.

The calculation is based on the assumption that the facility will operate at its maximum capacity 24 hours a day, year-round, with time set aside for maintenance and repairs. The uptime is approximately 96%, i.e. 8400h annual operating time. This allows for roughly two weeks of downtime every year, as imposed by PoE. PoE has set the annual input of silaged biomass to the plant to 3500 DM (dry matter) tonnes.

Table 3.2: Facility operation parameters

Facility Type	Chemical Processing
Operating Mode	Continuous Process
Operating Hours per Year	8400
Annual whole-crop input	3500 DM tonnes
Process Fluids	Liquids, Gases, and Solids

3.6 Product Design Specification

A product design specification (PDS) is "a statement of what a not-yet-designed product is intended to do" (The Open University, 2001). By applying PSD, it is ensured that the subsequent design and development of a product will meet the needs of the purchaser. In other words, the PDS is a specification of what is required but not the specification of the product itself. It acts as an initial boundary in the development of products (The Open University, 2001). In terms of product purity for this study, the following objectives were defined as minimum requirements, which the simulations aimed to fulfil:

- **Protein concentrate**: An example of a study performed on the production of bean protein concentrate was used as a guide for our concentrate purity. The study (Kohnhorst et al., 1991) shows most of the concentrates from beans with 80-83 wt% protein. Therefore, the composition of the concentrate obtained by the simulations is intended to approach the values of the concentrate specification shown on this article.

- **Dextrose:** Typical values for dextrose monohydrate purity sold as a starch-derived sweetener is 99% dextrose on dry basis. Furthermore, a maximum of 9.5% moisture content and 0.03% ash content are desired (Hobbs, 2009). These values are assumed as target for the simulation.
- **Ethanol**: Because of the azeotropic properties of an ethanol-water solution, the distillation process can practically produce an ethanol-water solution that is purified to the maximum of approximately 95% ethanol and 5% water (Vander Griend, 2007). A target purification of 90% is set for the simulations in this study, assuming that a dehydration process will later be added to increase purity to >99% to reach fuel ethanol requirements for blending with gasoline (Taherzadeh & Karimi, 2008).
- **Briquettes**: Moisture content in the briquettes ready to be sold should be about 12 wt% (Grover & Mishra, 1996). Since stalks and hulls are already assumed to have a 10% moisture content obtained by natural drying (lab analyses performed sometime after ensiling showed this moisture content), further drying is not simulated. As for the material size, due to the lack of information on the feedstock particle size distribution, simulations of the solids shredding and grinding are not performed. The focus on the simulations is rather given to the heating requirement of the briquetting or densification step.

3.7 Feedstock Composition and Mass Flow Rates

In general terms, the composition and moisture of legumes is subject to a number of factors (e.g. bean variety, region, weather, soil type, fertilization practices, harvesting and storage practices, time in storage, among others) and can therefore vary to a great extent (Crépon et al., 2010).

In this study, calculations and simulations were performed for a specific feedstock according to the data provided by PoE project. PoE provided this study with the compositional analyses of a sample of ensilaged biomass from a harvest of the legume specie *Faba bean,* also called *broad bean.* Moreover, lab analyses of the three fractions after processing the aforementioned ensilaged crop through the wet thresher were also provided.

Table 3.3: Dry matter Composition of each fraction out of wet thresher

Composition on Dry basis (g/kg)	**Bean fraction**	**Stalk fraction**	**Extract fraction**
Protein	257	126	734
Starch	450	-	-
Sugars	-	7	5
Fibre	206	-	-
Cellulose	-	171	-
Hemicellulose	-	334	-
Lignin	0	6	-
Ash	33	108	261
Oil	9	-	-
Solunkn*	45	247	-

**Solunkn: Unknown soluble solids*

Where the mass balance did not sum to 100%, the “unknown soluble solids” component was used to close it by difference. This measure was observed to be applied by Wooley et al. (1999) on their simulations for ethanol production processes, thus it was accepted as valid for the present case.

It must be considered that some assumptions and calculations were required prior to simulations in order to adapt the limited available experimental data and properties to the broader data requirements of the simulation software. First, in order to obtain the moisture content of each fraction, some assumptions were made. The reason for this is that compositional analyses performed on the three fractions were performed some time after the fractions separation, which meant that all fractions – even if mainly the stalks and the extract fractions – had dried. Consequently, the water content directly after the wet thresher separation was not known when this study was performed.

PoE set the annual input of silaged biomass to the plant as 3500 DM tonnes. Based on that, Appendix B includes all the assumptions and mass balances that were required to start with the simulations. The obtained mass flow rates and moisture content of the three fractions out of the wet thresher are summarized in Table 3.4.

Table 3.4: Mass flow rates and moisture content of each fraction

	Bean Fraction	**Stalk Fraction**	**Extract fraction**
Mass flow rate (kg/h)	274.91	280.42	391.64
Moisture content (%)	18.19	40.00	94.00

3.8 Bean Fraction Pretreatment: Dehulling and Starch-Protein Separation

The main aim of this study is to represent the unit operations described by PoE project by simulations on Aspen Plus in order to predict its outputs and their respective composition. Bean fraction pretreatment, for example, showed to be a significantly complicated process step in terms of representation on the simulation software. This sub-section, thus, describes the approach and design basis applied to simulate bean pretreatment on Aspen Plus. Furthermore, the following sub-sections in Chapter 3 describe the approach followed in each unit operation of the technology in order to build a simulation model as true as possible to PoE description.

3.8.1 Bean Fraction Pretreatment described by PoE

In order to separate the starch and protein fractions in the bean grains, the beans need to be first dehulled. According to PoE, the hulls of the beans have mostly been open during ensilage but not separated from the bean. In order to completely separate the seeds from the hulls, the beans pass in between polyurethane (PU) rollers, which make the two parts fall apart. Since hulls are lighter than bean seeds, they are then separated in a liquid bath. Hulls are lighter and float, while seeds are heavier and sediment to the bottom of the liquid. Next, beans are ground with an ultra mixer. The obtained bean flour contains two distinct groups of particles based on both their size and density. First, the light fraction of the bean flour is rich in protein and, second, the heavy fraction is rich in starch. Because of the difference in their size and density, starch-protein separation is done by means of sedimentation in a decanter. First, the bean flour is mixed with a so-called transfer solution in a collector. The transfer solution is one of the process streams, more specifically, the stream outlet from the saccharification vessel. The transfer solution consists of water mixed with glucose and small quantities of other compounds, causing a specific gravity (density) of approximately 1.15 g/cm^3. The separation of starch and protein consists of the solubilization of protein and the sedimentation of starch granules contained in the bean flour. The starch-rich fraction settles due to its average density (1.5 g/cm^3) being greater than that of the protein particles (1.1 g/cm^3) (Biss and Cogan 1988; Gausman et al. 1952; Steinke & Johnson 1991) and than that of the transfer solution. On the contrary, most of the protein remains soluble and appears floating on the surface of the transfer solution due to its lower density, while a smaller part of the protein settles with the starch fraction. After the sedimentation step, most of the protein content is skimmed by mechanical means from the surface of the transfer solution and sent to the protein coagulation tank. The used transfer solution is then recycled to the fermentation vessel. As a result, two new streams are produced: the protein-rich solution (the light fraction) and the starchy slurry (the heavy fraction).

3.8.2 Limitations on Available Data

As this study is an initial assessment of the PoE technology, there are limitations on the available data. On one hand, due to lack of experimental data on chemical composition distribution during beans dehulling for the present feedstock, and due to the absence of an appropriate unit on Aspen Plus software suitable to model this separation, assumptions were required. Experimental values found on the literature were used in order to assume the separation outcome, and the results of these assumptions were directly inserted on Aspen Plus. On the other hand, no experimental results at the time of this study on the separation efficiency of the sedimentation process were provided either. This process step was partly modelled by a decanter unit on Aspen Plus and partly user-specified. Finally, as the particle size distribution of the bean grains was unknown, beans were assumed as already milled to bean flour fot the input to Aspen Plus. This section gives details of all the assumptions.

3.8.3 Dehulling

As already mentioned, the mass flows and compositions of the streams obtained after beans dehulling were calculated supported by results of studies found during the literature review. Like that, the seeds stream and the hulls stream were directly inserted in the software as a feedstock to the plant. First, the dry matter on the beans fraction out of the wet thresher was divided into two sub-fractions, i.e. seeds fraction and hulls fraction. In order to do so, the typical dry matter distribution found by Jensen et al. (2010) for legumes dehulling was assumed as applicable.

Table 3.5: Dry Mass distribution on dehulling process (Jensen et al., 2010)

Seeds fraction (% of DM in bean fraction)	80.35 %
Hulls fraction (% of DM in bean fraction)	19.65 %

Secondly, the composition of each stream was also calculated with the help of results of previous compositional analyses on legume seeds found on the literature (Youssef et al., 1987; Mateos-Aparicio et al., 2010) performed before and after dehulling. These studies provided how much percent of each compound follows seeds and how much follows hulls when dehulling beans. When the % following each fraction was not given, some assumptions were applied by aiming to approach the final composition of seeds and hulls shown on the aforementioned studies. Table 3.6 presents the compositions and mass flows of the input streams on Aspen.

Table 3.6: Composition of each fraction after dehulling. Input to Aspen Plus

	Seeds composition (%)	**Hulls composition (%)**
Protein	25.33	3.42
Starch	43.76	8.43
Fibre	4.19	68.57
Solunkn	4.38	0.84
Oil	0.92	0.00
Ash	3.23	0.55
Water	18.19	18.19
MASS FLOW (kg/h)	220.86	54.05

3.8.4 Starch-Protein Separation

The best way to simulate sedimentation on Aspen Plus is assumed to be by using the so-called *decanter* block included on the software. The separation sharpness - slope of the separation curve - is specified and the model calculates a separation curve based on the settling velocity of the particles and the user input. Consequently, the governing classification characteristic is the settling velocity of the particles. However, the limitations on the available data meant that some assumptions were required in order to obtain more realistic results on the composition of the resulting streams out of the decanter unit.

The first limitation is that, since the fibre, starch and ash components of the bean flour are specified as “solids” in the software, these components are automatically sent to the heavy fraction out of the decanter, i.e. to the starch-rich fraction. However, according to the literature (Tyler et al., 1981), the lighter protein fraction floating on the surface of the transfer solution out of the decanter must have a relatively high content in soluble fibre and ash.

On the other hand, the second limitation is related to the mechanical skimming process used to separate the floating protein-rich fraction from the transfer solution after the decanter centrifuge. The decanter block provides stream results for one heavy fraction (which should represent the starch-rich) and one light fraction (the rest). However, the model library of Aspen Plus does not contain any specific model that can represent mechanical skimming processes, thus the separation of the protein-rich fraction from the glucose transfer solution had to be partly user-defined by the use of experimental data from literature (Tyler et al., 1981; Askar, 1986) in order to achieve a realistic process model.

3.9 Protein Concentrate Processing

In order to obtain the protein concentrate product, the liquid protein must be first coagulated in order to filter it and reduce its water content. After temperature conditioning (i.e. heating to the coagulation temperature, 80°C according to PoE) and in order to simulate the actual protein coagulation, a *RStoic* block is inserted on Aspen Plus. This block aims to represent a stoichiometric reactor. With this unit the phase change of protein is represented: from dissolved state (called *ProtSol* on the software) to precipitated-solid state (called *Protein* on the software). Like that, the subsequent filtration that is required in order to concentrate the protein can be modelled as a *CFuge* block, which represents a centrifuge filter on the software that separates solids from liquid. The solid protein-rich fraction out of the filtration step is finally further concentrated in an evaporator.

Table 3.7: Details of the reaction in coagulation reactor block

Reaction	**Reactant**	**Conversion of the reactant**
ProtSol(d) → Protein(s)	ProtSol	1.00

3.10 Starch-to-Glucose Process

In order to convert the starch content of the biomass into glucose monomers, three unit operations must be simulated on Aspen Plus: gelatinisation, liquefaction and saccharification.

3.10.1 General Parameters

Since gelatinisation is a phase transition of starch heated in the presence of sufficient water, the water content in the starch fraction entering the starch-to-glucose process needs to be initially adjusted. The starch concentration during gelatinisation is limited to 30–35 wt% dry solids, because higher concentrations cannot be processed in the screw/heat exchanger (Baks, 2007). More precisely, according to Lee et al. (2005) gelatinisation requires a moisture exceeding 66.7%, thus addition of water to the starch fraction stream is included in the simulations in order to adjust the water content to approximately 67%. Gelatinisation is thus simulated in a heat exchanger where the dilute starch fraction is heated until reaching the temperature of 83°C (suggested by PoE), temperature at which gelatinisation of starch chains occurs.

As for liquefaction, this process step should be represented by a reactor with the addition of alpha- and glucoamylases, which break the long starch chains into shorter ones. However, there is lack of data on the reactions occurring during starch liquefaction and the length of the partly-hydrolysed chains, i.e. the products of these reactions. As a consequence, simulation of liquefaction on Aspen Plus involves no rections. Instead, the subsequent saccharification reactor in the model (at 60°C and 1 atm) is used to represent the conversion rate of the overall reaction occurring between liquefaction and saccharification steps, i.e. the overall conversion of long starch chains to directly glucose monomers. The conversion rate of this reaction is the result of the action of enzymes, and it was obtained from the literature (Borglum, 1980).

Even if both liquefaction and saccharification steps require the addition of enzymes (alpha- and glucoamylases), but this aspect is not considered in the Aspen model due to lack of data on enzyme structure and its properties. Enzyme purchase is however considered in the economic assessment. The decision of obviating enzyme on Aspen model but including it in the economic assessment is assumed as reasonable, as ethanol plants generally purchase enzymes from outside suppliers, and enzyme recycling is currently not practiced (Dunn et al., 2012).

3.10.2 Stoichiometry

The reactions in the liquefaction and saccharification reactors could not be modelled with kinetic expressions. The reason for it is the low level of development of regression of experimental data within the field of conversion of starch contained in beans to ethanol. Instead, simulation of liquefaction step is simplified since no reactions involving the action of enzymes in breaking the starch long molecules are simulated on the software. In order to overcome this inaccuracy, the *overall* starch-to-glucose conversion efficiency (including both liquefaction and saccharification conversions) is set as a parameter in *RStoic* block that represents the subsequent saccharification step. The saccharification step is modelled with experimentally determined conversion of starch in broad bean found on the literature (Faulks & Bailey, 1990). The reaction stoichiometry and conversion rate input in the saccharification reactor is presented in Table 3.8.

Table 3.8: Details of the reaction in saccharification reactor block

Reaction	**Reactant**	**Conversion of the reactant**
Starch(s) + H_2O → Glucose(d)	Starch	0.80

3.10.3 pH Control

For the level of detail in this study, pH adjustments will not be accounted for in the simulations on Aspen Plus.

3.11 Lignocellulose Hydrolysis including Pretreatment

In Process Design 3, lignocellulose is hydrolysed in order to further convert it to ethanol. This sub-section presents the steps followed in order to simulate this new conversion on Aspen Plus.

3.11.1 General Parameters

In case the lignocellulosic biomass is used to produce bioethanol, a new stream line is entered in the Aspen file already developed for only starch-derived ethanol production, i.e. for Process design 2. This new stream includes weak-acid pretreatment and enzymatic hydrolysis of the present lignocellulosic biomass. Lignocellulosic biomass consists of both stalks and the hulls that had been previously separated from the bean grains.

Weak-acid pretreatment is simulated in a reactor, where stalks and hulls are mixed in a solid-to-liquid ratio of 1:6 and at 85°C temperature (Garcia et al., 2013). Pretreatment is used to sterilize the lignocellulose and almost totally dissolve the contained hemicelluloses. Furthermore, at these conditions some of the lignin is also solubilized and cellulose is “exposed” for subsequent enzymatic hydrolysis (Aden et al., 2002). According to TCBB, the partner in the PoE project in charge of running tests for lignocellulose hydrolysis, pretreatment is carried out with 1 wt% of nitric acid solution. However, the addition of this chemical compound is not included on simulations on Aspen Plus. Instead, the reaction conversion rate is directly inserted in the reactor block.

Next, the resulting slurry out of the pretreatment reactor, which contains the dissolved and solid lignocellulosic components, is sent to enzymatic hydrolysis after temperature conditioning in a heat exchanger. The goal for this unit is to dissolve most of the contained cellulose into glucose with the help of enzymes, since hemicellulose chains are already hydrolyzed in the pretreatment step (Garcia et al., 2013). As defined by TCBB during their experimental tests, enzymatic hydrolysis is simulated in a reactor at 55°C and 1 atm. The solids content is also adjusted before hydrolysis, since total solid content of the flow must be 20 ± 0.1 wt% (Aden et al., 2002). As for the case of starch-to-glucose conversion, due to lack of data on enzyme structure and properties, the simulation of hydrolysis steps will involve no enzymatic load. Instead, directly the conversion rates of the reactions – which are the result of enzymes action – are introduced in the software.

The research by TCBB to date has included weak-acid pretreatment, using a sample of bean stalks and a self-developed enzyme cocktail. This has been performed at lab scale to test enzyme activity, since the optimized enzymes are not yet available. The produced enzyme cocktail showed to hydrolyze both hydrocarbons present in the sample, i.e. cellulose and hemicellulose, with a conversion rate of 41.5%. Consequently, these preliminary results obtained by TCBB in the first run of experiments on stalks hydrolysis are used in this study. Nevertheless, it must be remarked that, according to the previsions by TCBB, the hydrolysis rate can be further optimized and higher conversions may be achieved.

3.11.2 Stoichiometry

In order to model pretreatment and enzymatic hydrolysis of lignocellullose on Aspen Plus, chemical reactions were obtained from a study on ethanol production from lignocellulose by NREL (Aden et al., 2002). The conversion percentage of available carbohydrate (including both cellulose and hemicellulose) that was successfully hydrolyzed into soluble sugars was obtained from the experimental results by TCBB. This means that data from Aden et al. (2002) and from TCBB were combined. Like that, side reactions during pretreatment and enzymatic hydrolysis were also included, together with the experimentally determined hemicellulose and cellulose conversion rates by TCBB for the specific feedstock of this study. The aim of combining these two sources is to provide a more realistic process model.

The experimental results by TCBB showed a 41.5% conversion of carbohydrates from bean stalks to liquor (into fermentable form) when using their enzyme cocktail together with weak-acid pretreatment. As side reactions, some degradation products are formed from pentose sugars (furfural), and from hexose sugars (hydroxymethyl furfural, HMF). Lignin is to a small extent dissolved during pretreatment, as well as starch is partly hydrolyzed to glucose due to the action of the acid. The reactions inserted on Aspen Plus and their respective conversion rates are shown in the following tables.

Table 3.9: Details of the reactions in weak-acid pretreatment reactor block

Reaction	**Reactant**	**Conversion of the reactant**
Cellullose(s) + H2O → Glucose(d)	Cellulose	0.050
Hemicellulose(s) + H2O → Xylose(d)	Hemicellulose	0.415
Lignin(s) → Lignin(d)	Lignin	0.050
Cellulose(s) → HMF(g) + 2 H2O	Cellulose	0.050
Hemicellulose(s) → Furfural(g) + 2 H2O	Hemicellulose	0.050
Starch(s) + H2O → Glucose(d)	Starch	0.300

Table 3.10: Details of the reaction in enzymatic hydrolysis reactor block

Reaction	**Reactant**	**Conversion of the reactant**
Cellullose(s) + H2O → Glucose(d)	Cellulose	0.365

3.12 Starch-derived Fermentation

This sub-section presents the details regarding fermentation of glucose sugars obtained from starch fraction in Process design 2.

3.12.1 General Parameters

Following the saccharification reactor, the slurry is transferred to the fermentation vessel. Fermentation is performed at 30°C and 1 atm under anaerobic conditions, with addition of *Saccharomicies cerevisiae* yeast. Glucose concentration of the resulting syrup from saccharification is controlled to a maximum of 20 ± 0.1 wt% sugars to avoid the production of high ethanol concentration. The reason for this is that ethanol is a growth inhibitor to yeast, thus a high ethanol concentration may lead to a large extent of the sugar undigested and wasted (Borglum, 1980). The ethanol concentration of the resulting solution out of the fermentation vessel is thus controlled to a maximum of 11 wt% (Easy Energy Systems, 2012).

As for the case of hydrolysis enzyme, the addition of yeast is not included in the simulations on Aspen Plus. Instead, the reaction conversion rate is directly inserted in the reactor block. This decision is assumed as reasonable since, even if it is possible to grow yeast on-site, this particular approach is in many cases costly and difficult due to the requirement of sterile reaction media and equipment (Knauf & Kraus, 2006). Moreover, it is uncommon for ethanol plants to recycle yeast (Dunn et al., 2012). The other alternative for ethanol plants is to purchase yeast from outside suppliers, and the yeast purchase is thus considered in the economic assessment on Chapter 6.

3.12.2 Stoichiometry

The fermentor vessel is simulated as an *RStoic* block and is modelled with experimentally determined conversions of specific reactions found on the literature. This type of modelling still satisfies the mass and energy balances. According to the results in some studies, it is expected that the remaining starch or the partly-hydrolyzed starch chains from saccharification continue being hydrolysed in the fermentation vessel due to the presence of remaining glucoamylase and alpha-amylase (Borglum, 1980). However, this "Simultaneous Saccharification and Fermentation" aspect is not modeled in this study. Starch-to-glucose conversion is rather simulated to take place fully in the saccharification reactor block, since this is how the conversion data for the whole starch-to-ethanol process was found in the literature (Borglum, 1980).

On the other hand, not 100% of the glucose is converted to ethanol and carbon dioxide during fermentation. In the typical fermentation conditions, there is ethanol loss due to carbohydrate used for yeast growth and for formation of small amounts of non-ethanol products, i.e. formation of acetaldehyde, methanol, butanol, acetic acid and glycerol (Franceschin, 2010). Consequently, the ethanol loss means that the yield is actually lower than the yield of stoichiometric formation of ethanol from glucose. According to the literature, glucose-to-ethanol fermentation will typically yield an 85% fermentation efficiency overall (Borglum, 1980) and, therefore, this conversion factor is used in the simulations. The side reactions are not included on the simulations due to lack of data (both experimental data and/or from the literature).

Table 3.11: Details of the reaction in starch-derived fermentation reactor

Reaction	**Reactant**	**Conversion of the reactant**
Glucose(d) $\rightarrow$ 2 Ethanol(d) + 2 CO_2(g)	Glucose	0.85

3.12.3 Micro-organism Growth

For the level of detail in this study, reactions for micro-organism growth and the related addition of nutrient sources will not be accounted for in the simulations on Aspen Plus.

3.13 Lignocellulose-and-Starch-derived Fermentation

In Process design 3, simultaneous fermentation of pentose and hexose sugars occurs in the fermentation vessel. The approach required to simulate this unit operation on Aspen Plus is described in this sub-section.

3.13.1 General Parameters

Following the enzymatic hydrolysis reactor where stalks and hulls have been processed, the resulting stream rich in pentoses and hexoses is transferred to the fermentation vessel. However, due to the presence of insoluble solids in the hydrolysate (which would hinder the fermentation rate) a *cyclone* block is required before fermentation.

The fermentation reactor block on Aspen Plus is the same one where the glucose-rich streams from starch saccharification are sent to. Therefore, fermentation of pentoses and hexoses coming from both starch and lignocellulosic feedstock is carried out in the same vessel.

It must be highlighted that own experimental data on co-fermentation of pentoses and hexoses of the feedstock for PoE project was not avilable at the time of this study. Consequently, data from literature was used instead. Fermentation is thus assumed to be performed at 41°C and 1atm, with addition of recombinant *Zymomonas mobilis* bacterium used as biocatalyst (Zhang et al., 1995). The total solids content in the reactor inlet is controlled to a maximum of 20 ± 0.1 wt%. In the study by Zhang et al., the organism *Z. mobilis* ferments both glucose and xylose to ethanol. On the other hand, even if it is known that some hydrolysis will occur during fermentation due to the action of remaining enzymes (glucoamylases and cellulases) in the solution, cellulose hydrolysis is modelled to take place entirely in the enzymatic hydrolysis vessel. This is due to the lack of a better understanding on the extent of hydrolysis occuring at fermentation conditions.

3.13.2 Stoichiometry

As experimental runs to get the yield of co-fermentation of pentoses and hexoses were not obtained at the time of this study, fermentation is modelled with conversion rates found on the literature (Aden et al., 2002; Zhang et al., 1995) in a *RStoic* block on Aspen Plus.

Table 3.12: Details of the reactions in co-fermentation reactor block

Reaction	**Reactant**	**Conversion of the reactant**
Glucose(d) → 2 Ethanol(d) + 2 CO_2(g)	Glucose	0.950
3 Xylose(d) → 5 Ethanol(d) + 5 CO_2(g)	Xylose	0.850
Glucose(d) → 3 Acetic acid(d)	Glucose	0.015
Xylose(d) + H2O → Xylitol(d) + 0.5 O_2(g)	Xylose	0.046
2 Xylose(d) → 5 Acetic acid(d)	Xylose	0.014

These conversion rates are based on the assumption that a total of 3% of the sugars available for fermentation are lost to contamination (Aden et al., 2002). This is modelled as a streams splitter, allowing the model to assign a percent loss to contamination. Like that, conversions in the fermentor model do not have to be adjusted.

3.14 Distillation

The fermentation product is processed in a two-step distillation process. The first distillation column facilitates the separation of the ethanol-water mixture from the slurry (i.e. the unconverted insoluble and dissolved solids). This is intended to lead to a distillate with an ethanol content of approximately 75 wt%. This step is followed by a rectification column that further concentrates the ethanol.

First of all, trays are employed as the sort of contacting device for the distillation columns since they are the most common contactor in use for this type of separation unit system (Katzen et al., 1997). Nutter V-grid trays are used for this purpose as these trays tolerate the solids well and have a relatively good efficiency (Aden et al., 2002).

The specifications of distillation columns were first estimated by using the *DSTWU* shortcut method included in Aspen Plus. This method employs the Winn-Underwood-Gilliland method, which provides an estimate of the minimum number of theoretical stages and reflux ratio, the feed stage, and the products split. By using this information together with the inlet streams composition obtained by Aspen, the rigorous calculation of distillation columns could be next performed using the *RadFrac* model of Aspen Plus (Quintero & Cardona, 2011). For our purposes, it is assumed that the towers have no pressure drop. The condenser and reboiler pressures are therefore set to 1 atm. As a summary, each column is designed from scratch and optimised as follows:

- Design specifications are entered in terms of recovery of ethanol in both the top and bottoms products. These specifications are input to the *DSTWU column* block in order to obtain the final column characteristics.
- Next, number of stages and feed stream stage are also specified according to results obtained by firstly applying the *DSTWU* method, which provides the minimum reflux ratio as well.
- Finally, for each design specification, a design variable must be specified on the *RadFrac* model. In this case, distillate rate and reflux ratio are specified.

Design of the columns is a tedious process that requires continuous adjustment. If there are any changes in the feed stream of the column, this design process must be repeated to re-optimize the column for the new feed.

Chapter 4

Description of Process Simulation on Aspen Plus

This section describes in detail the models on Aspen Plus software developed for the three plant configurations according to the different outputs.

4.1 Process Design 1

Three different process areas are found in this simulation: conversion of protein-rich streams to protein concentrate, conversion of starch-rich stream to purified dextrose, and conversion of lignocellulose to briquettes. Figure 4.1 on the upcoming pages presents the flowsheet developed on Aspen Plus for Process design 1.

4.1.1 Protein Concentrate Production

The extract liquid fraction from the wet thresher is one of the input streams to the model. First, this stream is mixed with the two protein-rich streams obtained during mechanical skimming of the floating protein in the starch treatment section (see Sub-section 4.1.2). The resulting mixture is heated (COAGHEAT) in order to reach protein coagulation temperature (80°C). Next, the heated stream is sent to the reactor (COAGULAT) where the coagulation of protein – change of phase from liquid to solid – is performed at the aforementioned temperature. The resulting stream is sent to filtration (FILTRAT). This block unit is a *CFuge* block, which represents liquid-solid separation using centrifuge filters. The resulting cake out of the filter enters a component separator (PRECIP) that represents the refining of the protein concentrate – removal of other solids such as starch, ash, or fibre. Last, the protein concentrate enters a *two-outlet flash* block (DRYER) that models the evaporation of part of the moisture content at 103°C.

4.1.2 Dextrose Production

The bean fraction out of the wet thresher is assumed as already dehulled and ground when input to Aspen Plus. Therefore, the ground seeds, which have the form of bean flour, are first mixed with the glucose solution – also called “transfer solution” by PoE, i.e. a part of the stream outlet from the saccharification vessel – and the mixture is sent to the sedimentation step (DECANTER). In the decanter block, a separation sharpness of 0.70 is specified. Next, two user-defined adjustments are required for both fractions out of the decanter. First, the heavy fraction goes through a component separator block (SOLIDSEP) where part of the solids are separated and will follow the light protein-rich fraction. Second, the light fraction goes through a component separator (PROSKIM1) that intends to simulate the mechanical protein skimming process. The skimmed protein is sent to the protein coagulation tank (COAGULAT). The used transfer solution is then recycled to the fermentation vessel and is thus sent to the collector of glucose-rich streams (MIXER3). As a result, two new streams have been obtained: the protein-rich stream (SKIPROT1) and the starchy slurry (STARCH1). The starchy slurry is mixed with water in order to lower its solids content before gelatinisation. The resulting stream is sent to gelatinisation, modelled as a heat exchanger (GELATINI) that warms the stream up to 83°C. The hot stream is then sent to a streams mixer (LIQUEFAC) that intends to represent the liquefaction step. Next, a second mechanical protein skimming is simulated, modelled as a component separator (PROSKIM2) as for the first skimming case. The resulting skimmed protein-rich fraction is sent to the protein treatment area. The liquefied starch stream (STARCH6) is cooled down to saccharification temperature (60°C) in a heat exchanger (COOLSTA). The stream enters the saccharification reactor (SACCHARI). The product stream (GLUCOSE1) contains the product, that is, the dextrose compound. The stream is further cooled down to 30°C in a heat exchanger (COOLGLU), and it is next split (SPLITTER) in two streams. Half of the glucose-rich stream (GLUCSEDI) is used as transfer solution, thus it is sent to the initial collector (TRASNMIX) used before the sedimentation step. The other half of the stream (GLUCOSE3) is sent to the collector of glucose-rich streams for dextrose purification (MIXER3). There, it is mixed with the recycled transfer solution. Dextrose purification process starts with a cyclone block (SOLIDRE1) for solids removal (e.g. non-converted starch, fibre, ash). Then, the refined stream (GLUCMIX2) enters the first evaporator (EVAP1) which is at 110°C. The concentrated stream (GLUCMIX3) is further refined in a component separator (SEPARAT2), and further concentrated in a second evaporator (EVAP2) at 122°C. The resulting stream out of the evaporator (SUGAR) contains the purified and dry dextrose.

4.1.3 Briquettes Production

Data on particle size distribution of the lignocellulosic part of the beans feedstock was not provided to this study. Consequently, briquettes production was very simplified in simulations. The lignocellulosic feedstock – both stalks fraction and hulls – with 10% moisture content is assumed to be already shredded and grinded in a hammer mill before entering the process on Aspen Plus simulations. The two lignocellulosic fractions are mixed and the mixture goes through a densification step (DENSIFIC). Densification is modelled as a heat exchanger at 160°C and 4bar.

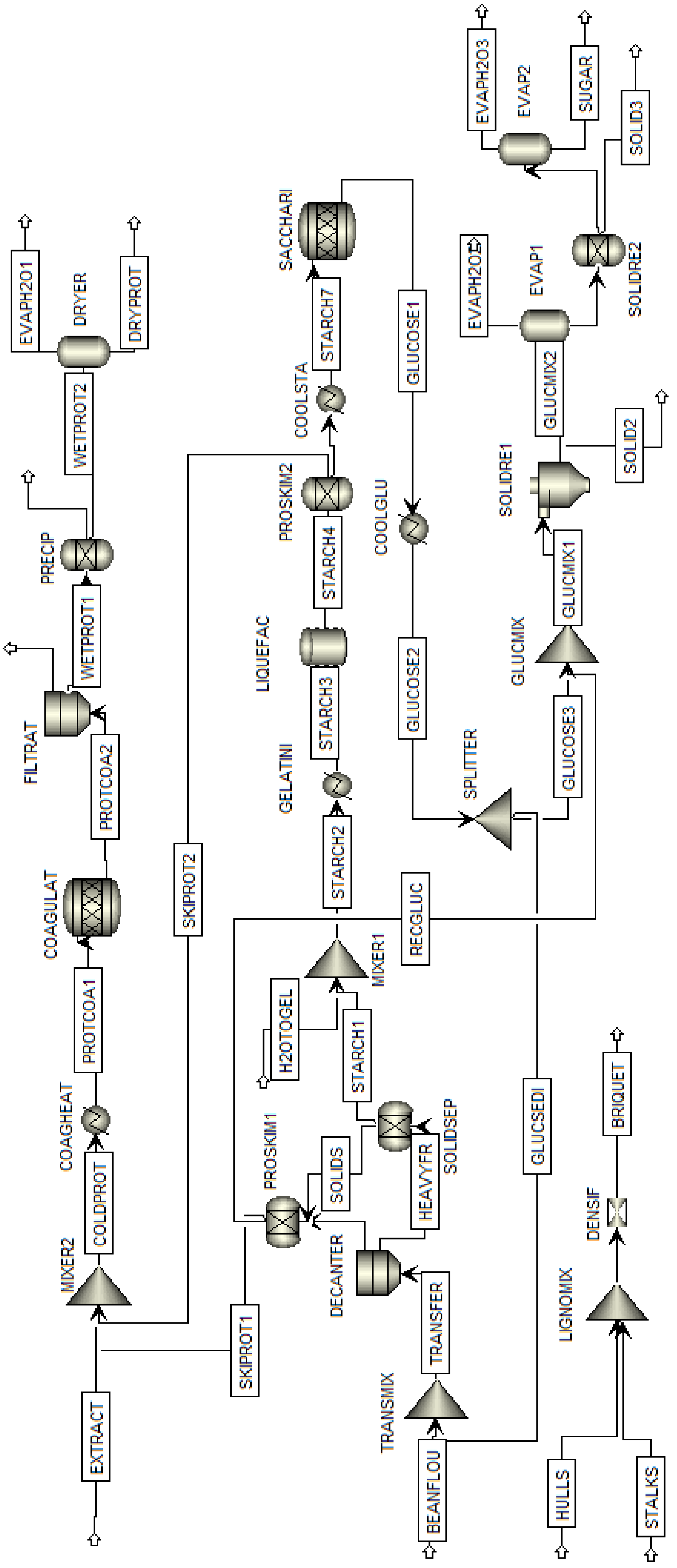

Figure 4.1: Aspen Plus flowsheet of Process design 1

4.2 Process Design 2

Three different process areas are found in this simulation: conversion of protein-rich streams to protein concentrate, conversion of starch-rich stream to ethanol, and conversion of lignocellulose to briquettes.

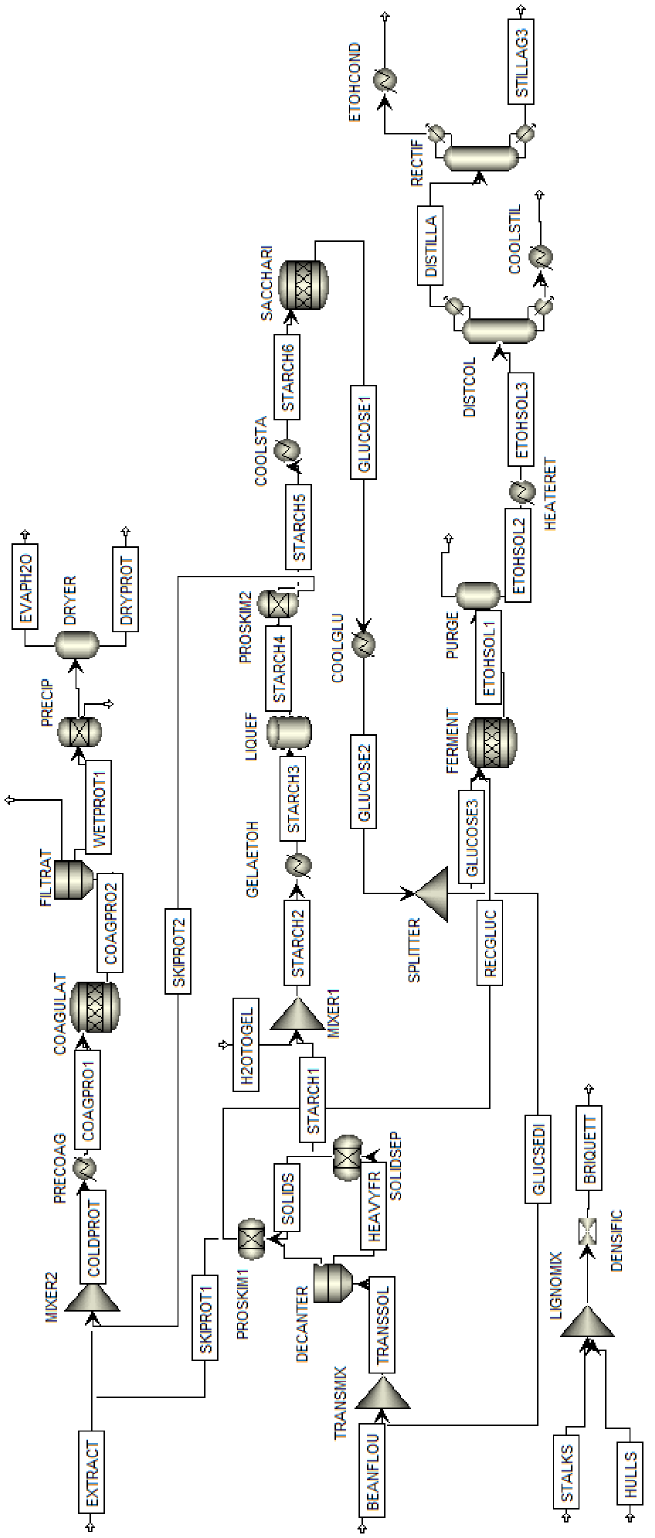

Figure 4.2: Aspen Plus flowsheet of Process design 2

4.2.1 Protein Concentrate Production

The simulation on Aspen Plus of the protein concentrate production line is exactly the same as for Process design 1.

4.2.2 Starch-derived Ethanol Production

This process is exactly the same as for Process design 1 until the unit for glucose-rich streams splitting (SPLITTER). One of the output streams (GLUCOSE3) of the splitter is sent to the collector of glucose-rich streams (MIXER3). There, it is mixed with the recycled transfer solution, and the water content is adjusted according to fermentation requirements. The mixture enters the fermentation reactor (FERMENT), which operates at 30°C. The product stream contains CO_2 gas and is first sent to a flash drum (PURGE) to simulate the gas escaping that occurs in the fermentation vessel. In this way, the pressure in the vessel (atmospheric pressure) can be kept constant. The flash drum is at the same conditions (temperature and pressure) as the fermenter is. Next, the ethanol-rich stream is pre-heated to nearly distillation temperature in a heat exchanger (HEATERET), that is, to 77.5°C. The stream enters the first distillation column (DISTCOL). The distillate obtained is then sent to the next distillation column (RECTIF). The bottoms of the first column are cooled down to 50°C in a heat exchanger (COOLSTIL). The second distillation column (RECTIF) has two output streams: the distillate, i.e. the final ethanol product (ETOHVAP), and the bottoms (STILLAG3). The ethanol stream is condensed in a heat exchanger (ETOHCOND) down to the stream’s bubble point.

4.2.3 Briquettes Production

The simulation on Aspen Plus of the briquettes production line is exactly the same as for Process design 1.

4.3 Process Design 3

Three different process areas are found in this simulation: treatment of proten-rich streams to protein concentrate, treatment of starch-rich stream to ethanol, and lignocellulose treatment to ethanol.

4.3.1 Protein Concentrate Production

The simulation on Aspen Plus of the protein concentrate production line is exactly the same as for Process design 1.

4.3.2 Starch Fraction Treatment

This process is exactly the same as for Process design 1 and 2 until the cooling unit (COOLGLU) for the product stream out of saccharification. In this design, the stream is cooled to 41°C, which is the new fermentation temperature. Then, it is directed to the stream splitter. One half of the glucose-rich stream is sent to the decanter block after the splitter. The other half (GLUCOSE3) is sent to the collector of glucose-rich streams (MIXER3). There, it is mixed with the recycled transfer solution, and with the stream rich in hexoses and pentoses from lignocellulose treatment (C5ANDC63).

4.3.3 Lignocellulose Fraction Treatment

Hulls and stalks are first mixed and, next, the water content of the mixture is adjusted in a stream mixer (MIXPRET) according to the pretreatment requirements. The mixture is heated to 85°C and sent to the pretreatment reactor (PRETREAT). The reactor product needs further water content adjustment. The stream is then cooled to enzymatic hydrolysis temperature (55°C) in a heat exchanger (COOLIGNO) and enters the hydrolysis reactor (ENZYHYDR). Next, lignin and some other solids need to be removed from the stream before entering fermentation, and this is done in the *Sub-stream splitter* block of Aspen Plus (LIGNOSEP). Finally, a 3% of the remaining stream is removed in a stream splitter (CONTAMIN), which aims to represent the 3% of losses by contamination that are accounted on the fermentation conversion rates.

4.3.4 Fermentation and Ethanol Purification

In a stream mixer (SUGARMIX), all the streams containing fermentable sugars are mixed before fermentation. The mixture is first cooled down to 41°C, the fermentation temperature, in a heat exchanger (SUGARCOO). The cooled stream enters the fermentation reactor (FERMENT). After fermentation, the product stream contains CO_2 gas and is first sent to a flash drum (PURGE) to simulate the gas escaping that occurs in the fermentation vessel. The flash drum is at the same conditions (temperature and pressure) as the fermenter is. Next, the ethanol-rich stream is pre-heated to nearly distillation temperature (77°C) in a heat exchanger (HEATERET). The stream enters the first distillation column (DISTCOL). The distillate is sent to the next distillation column (RECTIF). The bottoms of the first column are cooled down in a heat exchanger (COOLSTIL) to 38°C. The second distillation column (RECTIF) has two output streams: the distillate, i.e. the final ethanol product (ETOHVAP), and the bottoms (STILLAG3). The ethanol stream is condensed in a heat exchanger (ETOHCOND) down to the stream's bubble point.

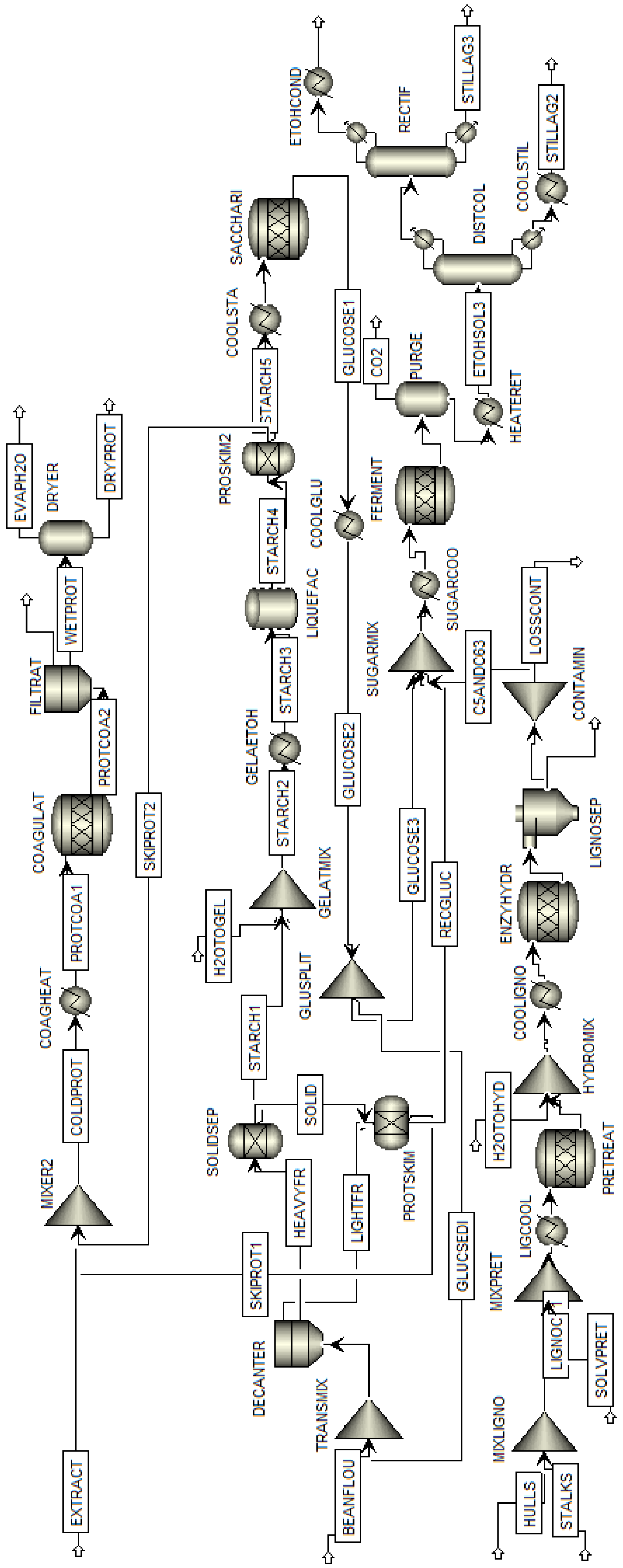

Figure 4.3: Aspen Plus flowsheet of Process design 3

Chapter 5

Heat Integration of the Ethanol Plant – Pinch Analysis

In Chapter 3, the importance of mass balances in process design was highlighted, as one of the main goals of simulations on Aspen Plus is to obtain the flow rates of the product outputs and make sure they accomplish the product design specifications. However, the availability of economical and reliable energy sources is essential for stable operation of the facility. Hence, an emphasis on efficient energy use at the facility - which will reduce the burden on required natural resources - is as interesting as the production rates of the outputs, in terms of plant design.

Energy balances are the key design practice in order to find the potential energy savings and, consequently, potential economic savings of the proposed design. Energy balances help in understanding the energy flows and where there is abundance and scarcity of energy within the overall process. According to that, a pinch technology analysis is performed in order to optimize the energy use (heating and cooling) of the plant. Heat integration analyses of the two latter process designs, i.e. Process designs 2 and 3, are found to be of significant interest due to their large energy use. Since the cost for electrical energy (used generally for grinding and running electric motors) in the ethanol production process is usually a minor cost item compared to thermal energy requirements (Gildred/Butterfield Limited Partnership, 1984), electricity will not be included in the energy balances.

5.1 Background on Pinch Analysis

The object of the heat integration analysis is to analyse the heat distribution system within the plant. The process has several sinks and sources of heat at various qualities and quantities, and if some of them can be matched, the external utility load of the plant can be reduced. The result of this analysis will then be used to derive a heat exchanger network (HEN) to distribute the energy as economic as possible within the system (Bösch et al., 2008).

Up to now, the ability to optimise the use of energy in chemical processes has been successfully applied by mainly two methodologies: the Heat Exchanger Network Synthesis problem and the Pinch method. The first methodology is very useful to find the best possible solution for the heat exchanger network, but it is also limited in providing the information about the possibilities to modify the process to reduce its minimum energy consumption. On the other hand, pinch method or technology gives full control of the design to the engineer and helps in identifying the parameters of the process that limit the energy savings. For this reason, Pinch technology is a very well-established tool for HEN design (Martin & Mato, 2008) and will be used for heat integration of the present cases.

Based on thermodynamic principles, Pinch technology offers a systematic approach to optimum energy integration in a process. This is done through setting an energy target for the design, i.e. the minimum theoretical energy demand for the overall process. Firstly, the energy targets for the process can be set without having to design the heat exchanger network and utility system. These energy targets can be calculated directly from the material and energy balance (Smith, 2005). Secondly, the objective of this technology is to match cold and hot process streams with a network of exchangers in order to reach the aforementioned energy targets. To do so, Pinch technology establishes a temperature, i.e. the pinch point, which separates the overall operating temperature region observed in the process into two temperature regions. At this temperature, driving forces for heat transfer are minimal and the heat transfer is equal to zero. Above Pinch temperature, there is a temperature region with heat deficit that must be covered by heating. Below Pinch, there is correspondingly a temperature region with heat surplus that must be removed by cooling. According to pinch method, it is not profitable to transfer heat from a deficit region (above Pinch) to a surplus region (below Pinch). Such a methodology will maximize the heat recovery in the process with the establishment of a heat exchanger network based on pinch analysis principles. Once Pinch analysis is performed, the best design for an energy-efficient heat exchanger network will result in a trade-off between the energy recovered and the capital costs involved in this energy recovery, i.e. in the heat exchangers network itself (Smith, 2005; Gundersen, 2000).

To summarise, the understanding of Pinch analysis gives three rules that must be obeyed in order to achieve the minimum energy targets for a process: (1) Heat must not be transferred across the pinch; (2) there must be no external cooling above the pinch; and (3) there must be no external heating below the pinch. Violating any of these rules leads to cross-pinch heat transfer resulting in an increase in the energy requirement beyond the target (March, 1998).

The following network design process will intend to satisfy these rules. However, often practical constraints prevent the theoretical assumption that any hot stream can be matched with any cold stream providing there is feasible temperature difference between them (Smith, 2005). There are many design-related reasons why constraints might be imposed. For example, a reason for a constraint might be that a stream can only exchange heat in maximum 2 or 3 heat exchangers (either with process streams or external utilities) in order to avoid unacceptably complex heat exchanger networks for a small-scale plant, as it is the present case. Also, potential control and start-up problems might call for constraints, e.g. in distillation columns and reactors (see sub-section 6.2 for further details). In consequence, Pinch analysis will be altered by these constraints and their effect on the energy performance of the plant will be evaluated using the Pinch method itself together with a little common sense.

Finally, even if the calculations required by the Pinch method are conceptually simple and can be done by hand, they become tedious and time-consuming if applied to a real-scale problem as the present case. Consequently, a computer software that performs those repetitive tasks was used. The ASPEN package that was available for this study did not include heat integration tools when streams with solid phase were present, thus pinch analyses were separately performed on the software called HINT (Heat Integration). HINT® is a free piece of educational software for HEN design based on the Pinch method developed by professors in the University of Valladolid (Martin & Mato, 2008). Detailed analyses, determining the energy recovered versus the capital cost involved, are not done for the process designs in this study, but is recommended for more detailed designs in the future.

5.2 Pinch Analysis of Process Design 2

The first task in applying a pinch analysis is to extract the required thermodynamic data for construction of the composite curves. All the process streams that undergo an enthalpy change need to be identified, i.e. all the 'hot' streams (those that need cooling) and 'cold' streams (those that need heating) of the process (Shing et al., 1997). The required thermodynamic data refers to stream flow rates, thermal properties, phase changes, and temperature ranges through which they must be heated or cooled. These data can only be obtained after mass balances have been performed and temperatures and pressures have been established for the process streams.

For process design 2, eighteen streams were identified as having a change in their enthalpy. The corresponding heat duties, specific heat capacity flow rate (mCp) and start and target temperatures of each stream were thus obtained from simulations on Aspen Plus. Only the start and target temperatures are displayed due to confidentiality constraints.

Table 5.1: Thermal data for hot streams in Process design 2

ID	HOT STREAMS	T_{start} (°C)	T_{target} (°C)
H1	Glucose cooling after saccharification	60	30
H2	Starch cooling after liquefaction	83	60
H3	Ethanol product condensation*	78.1	50
H4	Stillage cooling for first distillation column	101.2	50
H5	Fermentation	30	30
H6	Condenser in first distillation column	82.4	82.4
H7	Condenser in rectifier column	78.1	78.1

The only stream (excluding distillation columns) with phase change is H3. The cooling process for this stream starts at the stream's dew point and finishes at its bubble point, thus the stream does not need to be broken up into dummy streams of different mCp values, but a constant mCp value may be assumed as approximated enough (King et al., 1999).

Table 5.2: Thermal data for cold streams in Process design 2

ID	COLD STREAMS	T_{start} (°C)	T_{target} (°C)
C1	Starch heating during gelatinisation	21.8	83
C2	Ethanol pre-heating before distillation	30	77.5
C3	Protein heating for coagulation	37	80
C4	Heating of solid part of wet protein	80	103
C5a	Heating of water content in wet protein up to boiling point	80	100
C5b	Evaporation of water content in wet protein dryer	100	100
C5c	Superheating of vapor in wet protein dryer	100.1	103
C6	Densification - Heating of lignocellulose	30	160
C7	Saccharification	60	60
C8	Reboiler in first distillation column	101.4	101.4
C9	Reboiler in rectifier column	84.3	84.3

Streams C4, C5a, C5b and C5c belong all to the streams entering and leaving the protein dryer. Due to different mCp values in this stream, it was required to break it up into dummy streams of different mCp values and latent heat in order to have a more realistic set of extracted data (King et al., 1999).

Diagrams on Figures 5.1 and 5.2 were sketched in order to have a clearer picture of the most significant heat sinks and sources within the process.

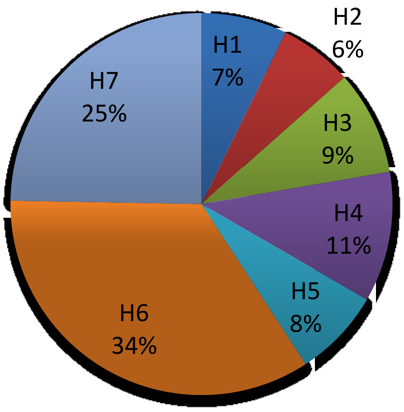

Figure 5.1: Cooling duty shares of each hot stream out of the total cooling demand

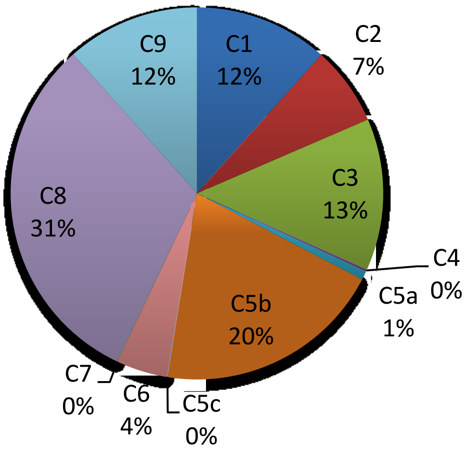

Figure 5.2: Heating duty shares of each cold stream out of the total heating demand

As it may be observed, H6 and H7 play the most important roles in cooling requirements. These two streams represent the condensers in the distillation columns. As for cold streams, the streams with higher heating demands are C8 and C5b, which are the reboiler in the first distillation column and the water evaporation in the protein concentrate dryer, respectively.

Also, the following utilities are assumed as available: medium pressure steam (6.90 bar) at 170°C and cooling water at 20°C that can be heated to 25°C. No chilled water is used in the plant since the required process temperatures can be achieved by cooling water year-round.

Next, the second task of the Pinch analysis is to choose the minimum allowed temperature difference in the heat exchangers, ΔT_{min}. The best design for an energy efficient heat exchange network will often result in a trade-off between equipment and operating costs, and this is dependent on the choice of the ΔT_{min} for the process. The lower the ΔT_{min}, the lower the energy costs, but the higher the heat exchanger capital costs, as lower temperature driving forces in the network will result in the need for greater area. On the other hand, a large ΔT_{min} will mean increased energy costs as there will be less overall heat recovery, but the required capital costs will be less (March, 1998). For this study, a 10ºC temperature difference is assumed as reasonable (see examples in Smith (2005)).

i. Pinch analysis without integration of distillation columns nor reactors

In pinch methodology, some heat duties may not be included in the network analysis because they are handled independently of the integration. As already mentioned, from process control considerations, constraints may arise in respect to some streams integration. As for the present case, one does not want to integrate the distillation column and the reactors unless it results in considerable energy savings. Thus, the duties of reboilers and condensers will be kept outside the preliminary analysis, as well as the saccharification and fermentation reactors (i.e. streams H5, H6, H7, C7, C8 and C9). It will later be analysed if integration of the distillation columns and reactors with the rest of the process does produce any savings in this particular case.

The energy targets (minimum heating and cooling utilities) are obtained using a tool called “Composite Curves”. The software HINT was used in order to draw the Composite Curves for heating and cooling, which also allow identifying the heat recovery pinch temperature for the process. Information on 12 streams from tables 5.2 and 5.3 (all streams except for the 6 streams mentioned above) was entered on the software as well as the minimum allowed temperature difference, ΔT_{min} = 10ºC.

The Composite Curves are established by adding the enthalpy changes for the streams in each temperature region (separately for the hot and the cold process streams). The overlapping region on the enthalpy axis represents the amount of available heat recovery, while the parts of the Composite Curves that extend outside the overlapping region must be covered by utilities for external heating and cooling. The temperature at which the specified minimum temperature difference (ΔT_{min}) is obtained is called Pinch temperature.

The information that can be subtracted from the Composite Curves (see Figure 5.3) is the following: Pinch temperature (hot and cold), minimum hot utility consumption, minimum cold utility consumption, and potential energy savings.

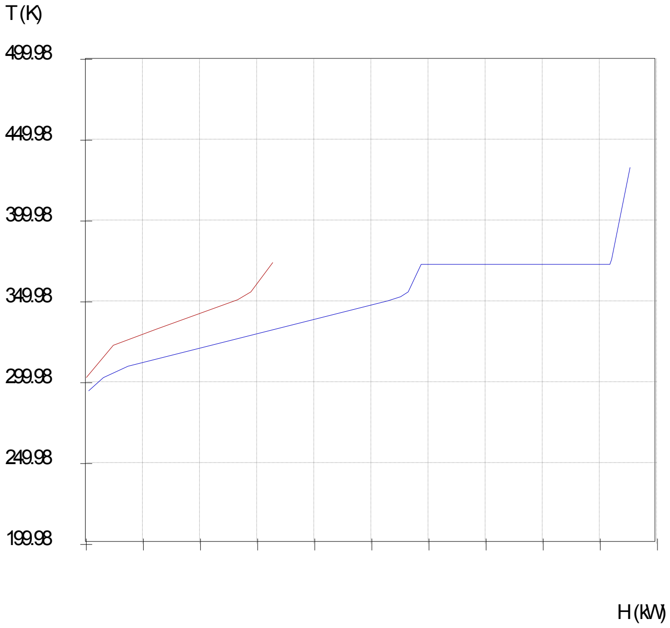

Figure 5.3: Composite curves for Process design 2

**See that x-axes labels of all graphs in this report have been removed in order to keep the results of this study confidential.*

Table 5.3: Pinch temperature

T_{pinch} (°C)	26.8
$T_{pinch\ hot}$ (°C)	31.8
$T_{pinch\ cold}$ (°C)	21.8

In order to estimate the minimum (or fewest) number of heat exchangers ($U_{min,MER}$) that is required to realize a heat recovery system, one must divide the network in two independent problems: one above and one below the pinch. This network is called Maximum Energy Recovery (MER) network, and its minimum number of units is given by the following equation:

$$U_{min,MER} = (N - 1)_{above\ Pinch} + (N - 1)_{below\ Pinch}$$

Where N is the total number of process streams and utility types above and below the pinch, respectively. This equation is developed by assuming that each heat exchanger is made as large as possible (which will normally result in a reduction of the number of units) in such a way that at least one of the streams has its total heating or cooling requirement satisfied (Gundersen, 2000).

In order to identify the total number of process streams and utility types above and below the pinch, the so-called Stream Grid tool is used. This representation (where the hot and cold process streams and utilities are drawn in a counter-current manner) is also the most common design environment for heat exchanger networks. Here, Pinch decomposition is obvious and driving forces in the hot and cold ends of the heat exchanger can be easily checked (Gundersen, 2000). The Stream grid for this process design is obtained by HINT and is shown in Figure 5.4 (see that the suitable matches that are found on the next step are directly incorporated in this figure).

The total number of process streams and utility types above and below the pinch is hence calculated from Figure 5.4: $N_{\text{above pinch}} = 13$ and $N_{\text{below pinch}} = 2$. As a consequence, in order to apply a heat recovery system where only the minimum hot and cold external utilities previously calculated are required, the *minimum* number of heat exchanger units (including both matches between process stream and matches with external utilities) is the following:

$$U_{\text{min,MER}} = (13 - 1)_{\text{above Pinch}} + (2 - 1)_{\text{below Pinch}} = 13$$

At this point, a MER heat exchanger network can be designed by using the Pinch Design Method. The method involves some ground rules or strategy for setting up the heat exchanger matches between the process streams.

The strategy of Pinch method suggests starting to find matches at the Pinch region, since the pinch is the most constrained region of the problem due to the restrictions in possible matches that ΔT_{min} imposes. Quite often there are essential matches to be made, but if such matches are not made, the result will be an excessive use of utilities resulting from heat transfer across the pinch (Smith, 2005). Furthermore, for temperature feasibility of the matches close to the pinch, the mCp value of the streams going out of the pinch needs to be greater than the mCp value of the stream coming into the pinch. Thus for temperature feasibility there is a "mCp rule":

$$\text{Above Pinch: } mCp_{Cj} \geq mCp_{Hi} \quad ; \quad \text{Below Pinch: } mCp_{Hi} \geq mCp_{Cj}$$

Like that, the streams diverge from ΔT_{min} and the match is feasible.

Above Pinch, where there is heat deficit, the main task is to cool the hot streams to Pinch temperature without the use of external cooling, in order to maximize the use of the limited heating resources. Because there is a requirement for minimum driving forces (ΔT_{min}), each cold stream can only cool one hot stream to Pinch temperature. Correspondingly below Pinch, where there is heat surplus, the main task is to heat the cold streams to Pinch temperature without the use of external heating, in order to maximize the use of the limited cooling resources. For driving force reasons, each hot stream can only heat one cold stream to Pinch temperature. Thus, the following must be satisfied with respect to the number of streams above and below Pinch:

Above Pinch: $n_C \geq n_H$; Below Pinch: $n_H \geq n_C$

Here, n_H and n_C are the number of hot and cold process streams that are present at the actual Pinch points. Following these restrictions, the matches found are the so-called *Pinch Exchangers*, which are those units where either (1) both the hot outlet temperature and the cold inlet temperature (above Pinch) or (2) both the hot inlet temperature and the cold outlet temperature (below Pinch) coincide with the hot and cold Pinch temperatures (Gundersen, 2000).

The results of the software calculations show that there is only one possible match for Pinch exchangers, and it is placed above the Pinch (since there is only one stream present below the pinch, no stream matches are possible in this temperature region). This match is between the streams H1-C1. Whenever a match is selected, its duty is maximized in order to reduce the number of units in the network. This simply means that the duty of the heat exchanger is set equal to the smaller between the cooling needed by the hot stream and the heating needed by the cold stream. This is called the "tick-off" heuristic, which steers the design toward the minimum number of units (Smith, 2005).

Occasionally, it appears not to be possible to create the appropriate matches to satisfy all the pinch streams above and below the pinch. The reason for this is that one or both of the two aforementioned design criteria for Pinch matches cannot be satisfied (i.e. rule for mCp value and rule for the number of hot/cold streams). In those cases, stream splitting is inevitable for a minimum utility design. In order to proceed with heat integration, hot and/or cold streams may be split into two (or more) branches, hence increasing the number of hot and/or cold stream branches at the same time as reducing the mCp values for the stream branches (Gundersen, 2000).

At this point, the first constraint on HEN design for the ethanol plants in this study is imposed: no stream splitting is allowed. As more splitting is done in a HEN design, additional cost of controlling the flow rates in each of the branches is added and, generally, a certain degree of complexity is inserted in the system design (Shah et al., 1988). And according to the inventor of PoE technology, one of the main attractions of the biorefinery is its design simplicity and simple operation and maintenance.

The second constraint on HEN design is that each stream can only pass through maximum 2 heat exchangers (where it exchanges heat with either other process streams or external utilities) in order to avoid unacceptably complex heat exchanger networks for a small-scale plant as the present case.

Once all the feasible Pinch Exchangers have been selected by respecting the multiple design constraints, the network must be completed by utilizing the rest of the heating resources in the hot streams above Pinch, as well as the rest of the cooling resources in the cold streams below Pinch (if present). The mCp inequality only applies when a match is made between two streams that are both at the pinch. Away from the pinch, temperature differences increase, and it is no longer essential to obey mCp inequalities. Thus, in these process-process heat exchangers, the inequalities for mCp values do not strictly apply, and the designer can discriminate on the basis of e.g. operability or plant layout (Gundersen, 2000).

Due to the external design constraints imposed by the technology inventor, only four feasible matches between process streams could be selected. Consequently, the hot stream H4 could not be completely cooled by other process streams to its target temperature, and one of the pinch methodology rules was not fulfilled. As a result, external heating is needed above the pinch, and the minimum hot and cold utilities consumption obtained in the Composite Curves cannot be reached. The resulting HEN is not a MER network and involves more heat exchanger units than the minimum number of units for MER network. Notwithstanding, the obtained external utilities demand for this network proposal is very close to the minimum value in case of MER network.

Table 5.4: Matches between process streams above pinch suggested for Process design 2 without integration of distillation columns or reactors

Match	**Description of the streams in the match**	**Match**	**Description of the streams in the match**
H1-C1	Glucose cooling and starch heating for gelatinisation. Starch needs external heating	H3-C3	Ethanol product condensation and protein heating for coagulation. Protein needs external heating
H2-C2	Starch cooling and ethanol pre-heating before distillation	H4-C2	Stillage cooling and ethanol pre-heating before distillation. Stillage needs external cooling

The other 9 heat exchanger units required are related to the satisfaction of the remaining heating demand of all the cold streams by the use of external utilities, and the remaining cooling demand of streams H4 and H1 by external cooling. These 9 units are depicted as red and blue circles on the Grid Diagram.

However, in reality, streams C4, C5a, C5b and C5c above pinch constitute the protein dryer and may be counted as a single stream with one single match with external heating utility. As for temperatures below pinch, there is no possibility for a match between process streams as it can be observed in Figure 5.4. As a result, in total, 10 heat exchanger units are required on the Grid Diagram by accounting for C4, C5a, C5b and C5c as a single stream.

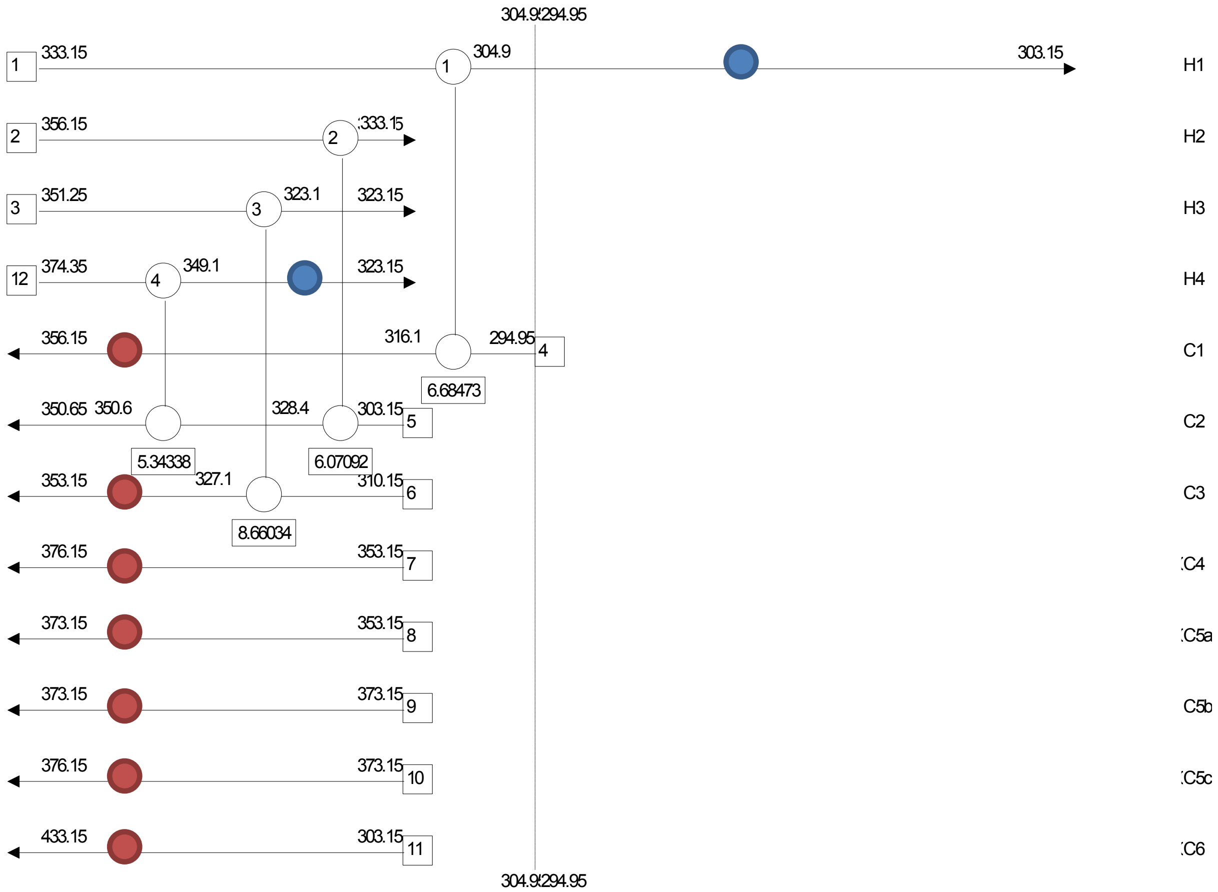

Figure 5.4: Grid diagram with streams, matches between process streams and utility matches for Process design 2

One must also consider the streams of the process that are not included in the Pinch analysis in order to obtain a complete picture of the heat exchanger network of this Process design. These streams include the reboilers and condensers in the distillation columns and the reactors, i.e. 6 streams. Thus the total number of exchanger units becomes 16 for this case.

ii. Pinch analysis with integration of distillation columns

Once the pinch temperature has been defined, integration of distillation columns and reactors may be discussed.

Regarding the distillation columns, appropriate column integration can provide wide energy benefits since these units are very energy intensive. However, these benefits must be compared against associated capital investment and difficulties in operation that column integration causes (Smith, 2005). Heat delivering from the condensers in the columns to the background process is only of interest if it happens in a temperature region where the process has heat deficit, i.e. above the pinch. Conversely, the reboilers in the columns could receive heat from the background process, but only if it happens in a temperature region where the process has heat surplus, i.e. below the pinch.

As for the reactors, integration of exothermic reactors is only of interest if it occurs above the pinch, i.e. where there is heat deficit. Alternatively, integration of endothermic reactors is only of interest if the temperature of the reactor is below the pinch. The following tables summarize the decision-making process for integration of these process units.

Table 5.5: Hot streams related to distillation columns and reactors

HOT STREAMS			
Unit	**Temperature (°C)**	**Above or below the pinch**	**Interesting for Integration**
Fermentation (exothermic)	30	Below	No
Condenser in distillation column	82.42	Above	Yes
Condenser in rectifier	78.10	Above	Yes

Table 5.6: Cold streams related to distillation columns and reactors

COLD STREAMS			
Unit	**Temperature (°C)**	**Above or below the pinch**	**Interesting for Integration**
Saccharification (endothermic)	60	Above	No
Reboiler in distillation column	101.44	Above	No
Reboiler in rectifier	84.26	Above	No

Since the condensers temperatures in both the distillation column and the rectifier (82.42°C and 78.104°C, respectively) are above the Pinch temperature (which for hot streams is 31.8°C), these condensers act as a heat source in the same region where the process has heat deficit. Consequently, there could be savings from integrating these units. However, integration of distillation columns with the rest of the process (the so-called “background process”) is only appropriate if the temperatures of the column’s processes lie on one side of the pinch (i.e. if the column is not placed across the pinch) and if the columns can be accommodated by the Grand Composite Curve (see below for explanation) of the background process (March, 1998). For this heat integration analysis, all reboilers and condensers temperatures lie above the pinch temperature of the background process, thus columns are appropriately placed.

Another aspect to consider is that, if both the reboiler and condenser of a column are integrated with the process, this can make the column very difficult to start up and control (Chen, 2007). Consequently, the option that better suits this problem is that, above the pinch, the reboilers are serviced directly from the hot utility and the condensers are intended to be integrated with the background process. In order to find whether the condensers can be fully or only partly integrated with the background process, the Grand Composite Curve of the background process is used. This graph is plotted by HINT software. The Grand Composite Curve is obtained from the Heat Cascade, which is constructed by establishing temperature intervals based on the supply and target temperatures for all the streams. A heat balance is then established for each of these temperature intervals based on heat delivered from the hot streams and heat removed by the cold streams within the interval. Finally, heat surplus in one interval is cascaded down to the next interval (Gundersen, 2000). If the medium temperatures in each temperature interval are plotted against the corresponding heat flows in the cascade, the Grand Composite Curve is obtained. Thus, the profile of the Grand Composite Curve represents residual heating and cooling demands after recovering heat within the temperature intervals in the Heat Cascade (Smith, 2005).

With this graphical tool, it can be readily observed how much heat can be exchanged at a certain temperature with the background process. In this case, at the temperature of the hottest condenser (i.e. 82.42°C or 355.57K), only a bit over half of the total condenser duty can be exchanged with other process streams (see purple horizontal line in Figure 5.5). Thus, not all the condenser duty can be exchanged with the background process. The reason for this is that large part of the required minimum hot utility must be provided at a higher temperature than the temperature of the condenser.

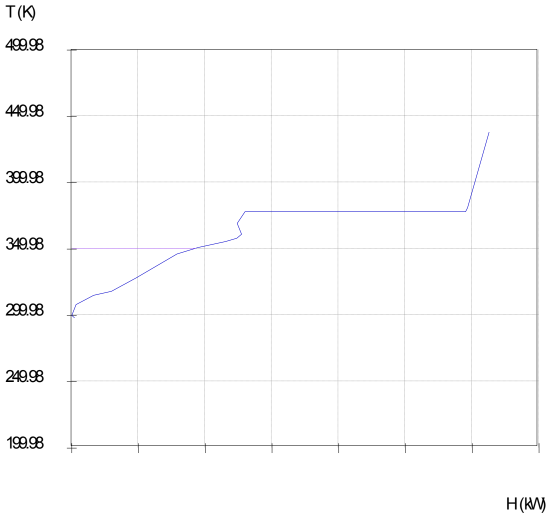

Figure 5.5: Grand Composite Curves for Process design 2

At this point, another constraint is applied to avoid complex heat integration arrangements for the sake of operability and control. This constraint imposes to perform the heat recovery from the condenser towards a single sink of heat, rather than towards two or three sinks of heat. If this constraint was not applied, difficult starts and control of the column would appear. According to that, a cold stream with a heat duty equal or higher than the duty of the condenser is the only possibility for a match with this part of the distillation column. Even by considering the duties of both condensers, there is no cold stream in the system that fulfils this condition except for stream C5b. However, stream C5b belongs to the protein dryer, i.e. it is just a part of the combined stream that enters and leaves the dryer unit. Subsequently, the eventual match between C5b stream and a condenser would lead to potential control problems. Moreover, the two streams are expected to be geographically distant from each other within the plant. For all these reasons, integration of distillation columns in this system does not seem a feasible improvement according to the constraints in plant design.

As a conclusion, the heat exchanger network proposed *without* integration of distillation columns shows to be the most appropriate for energy recovery in Process design 2. Table 5.7 presents the required number of heat exchangers for the proposed HEN, as well as the proportion of the actual energy savings obtained by the proposed HEN compared to the potential energy savings in MER network design. This value differs from 100% due to the variety of design constraints imposed. The total external heating and cooling loads were also obtained in line with the actual energy savings of the proposed HEN but are kept as confidential.

Table 5.7: Summary of key figures of proposed HEN for Process design 2

Proportion of actual energy savings obtained by the proposed HEN compared to the potential energy savings in MER network	82.99%
Number of matches between process streams	4
Total number of heat exchanger units	16

5.3 Pinch Analysis of Process Design 3

For process design 3, twenty-two streams were identified as having a change in their enthalpy. The corresponding heat duties, specific heat capacity flow rate (mCp) and start and target temperatures of each stream were obtained from the simulations on Aspen Plus. Only the start and target temperatures are displayed due to confidentiality constraints.

Table 5.8: Thermal data for hot streams in Process design 3

ID	HOT STREAMS	T_{start} (°C)	T_{target} (°C)
H1	Glucose cooling after saccharification	60	41
H2	Starch cooling after liquefaction	83	60
H3	Stillage cooling for first distillation column	101.7	38
H4	Ethanol product condensation	78	41.4
H5	Lignocellulose cooling after pretreatment	78.6	55
H6	Sugars cooling to fermentation temperature	51.83	41
H7	Fermentation	41	41
H8	Exothermic reactor	55	55
H9	Condenser in first distillation column	81.52	81.52
H10	Condenser in rectifier column	77.98	77.98

Table 5.9: Thermal data for cold streams in Process design 3

ID	COLD STREAMS	T_{start} (°C)	T_{target} (°C)
C1	Starch heating during gelatinisation	23.2	83
C2	Etanol pre-heating before distillation	41	77
C3	Protein heating for coagulation	37.4	80
C4	Heating of solid part of wet protein	80	102
C5a	Heating of water content in wet protein to boiling point	80	100
C5b	Evaporation of water in wet protein	100	100
C5c	Superheating of vapor in wet protein dryer	100	102
C6	Lignocellulose heating before pretreatment	21.56	85
C7	Saccharification	60	60
C8	Lignocellulose pretreatment	85	85
C9	Reboiler in first distillation column	101.75	101.75
C10	Reboiler in rectifier column	83.77	83.77

The following utilities are assumed as available: medium pressure steam (MP) at 175°C and cooling water at 20°C that can be heated to 25°C. Furthermore, a ΔT_{min} of 10°C is also assumed as reasonable for Process design 3.

Diagrams on Figures 5.6 and 5.7 give a picture of the streams with higher heating and cooling demands. As it can be observed on those Figures, for Process design 3, the largest cooling demand is *not* located in both condensers of the distillation columns as for the case of Process design 2. Now, it is the stream H3 which has the second largest cooling demand, i.e. the stream that represents the stillage cooling after first distillation column. As for cold streams, stream C9 represents almost half of the heating demand of the process, being this the reboiler of the first distillation column. The second largest heating demand lies in the stream C6, which represents lignocellulose heating to pretreatment temperature (85°C).

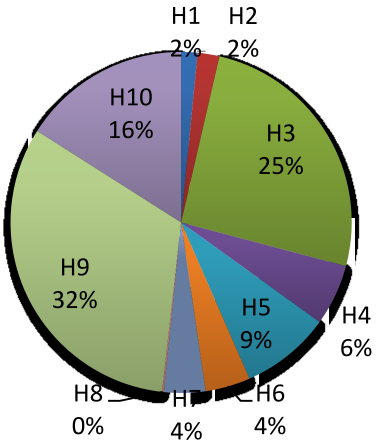

Figure 5.6: Cooling duty shares of each hot stream out of the total cooling demand

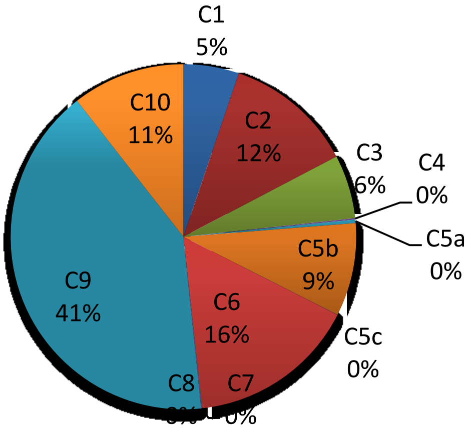

Figure 5.7: Heating duty shares of each cold stream out of the total heating demand

i. Pinch analysis without integration of distillation columns nor reactors

Due to the same reasons as for Process design 2, distillation columns and reactors will be kept outside of the preliminary analysis. Even if it can be readily observed that condensers and reboilers in Process design 3 represent large heating and cooling demands, for process design reasons a first HEN design without their integration is suggested. It will later be analysed if integration of distillation columns and reactors with the rest of the process does produce any savings in this particular case. In accordance with that, HINT simulations were performed to intend to design a MER exchanger network for Process Design 3. This resulted in a pinch analysis involving fourteen streams. The Composite Curves of these hot and cold streams combination were plotted by HINT.

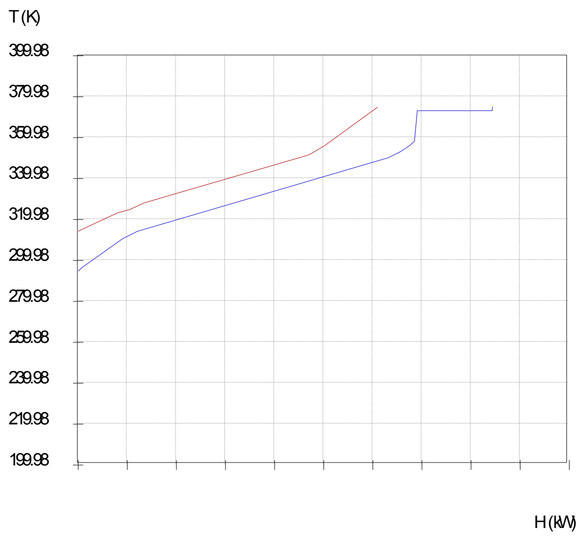

Figure 5.8: Composite Curves for Process design 3

Table 5.10: Pinch temperature

T_{pinch} (°C)	46.83
$T_{pinch\ hot}$ (°C)	51.83
$T_{pinch\ cold}$ (°C)	41.83

The Stream grid for this process design is also obtained by HINT and is shown in figure 5.9. The minimum (or fewest) number of heat exchangers ($U_{min,MER}$) that is required to realize a MER heat recovery system is, thus, calculated as the following: $N_{above\ pinch} = 15$ and $N_{below\ pinch} = 0$.

$$U_{min,MER} = (\ 15 - 1\ )_{above\ Pinch} = 14$$

The results of Pinch Design Method for MER heat exchanger network by HINT software show that there are no streams below Pinch, as well as no possibilities for Pinch exchangers. Therefore, the most appropriate non-Pinch exchangers are user-defined and their duties are maximized in order to reduce the number of units in the network. However, due to the system constraints of no stream splitting and maximum number of units per stream, three of the hot streams (streams H4, H5 and H6) could not be completely cooled to their target temperature. This leads to energy savings that are considerably lower than the potential energy savings for MER heat exchanger network.

Table 5.11: Matches between process streams above pinch suggested for Process design 3 without integration of distillation columns or reactors

Match	**Description of the streams in the match**	**Match**	**Description of the streams in the match**
H1-C1	Glucose cooling and starch heating for gelatinisation. Starch needs external heating	H3-C3	Ethanol product condensation and protein heating for coagulation
H2-C2	Starch cooling and ethanol pre-heating before distillation. Ethanol needs external heating	H3-C6	Stillage cooling and lignocellulose heating before pretreatment. Lignocellulose needs external heating

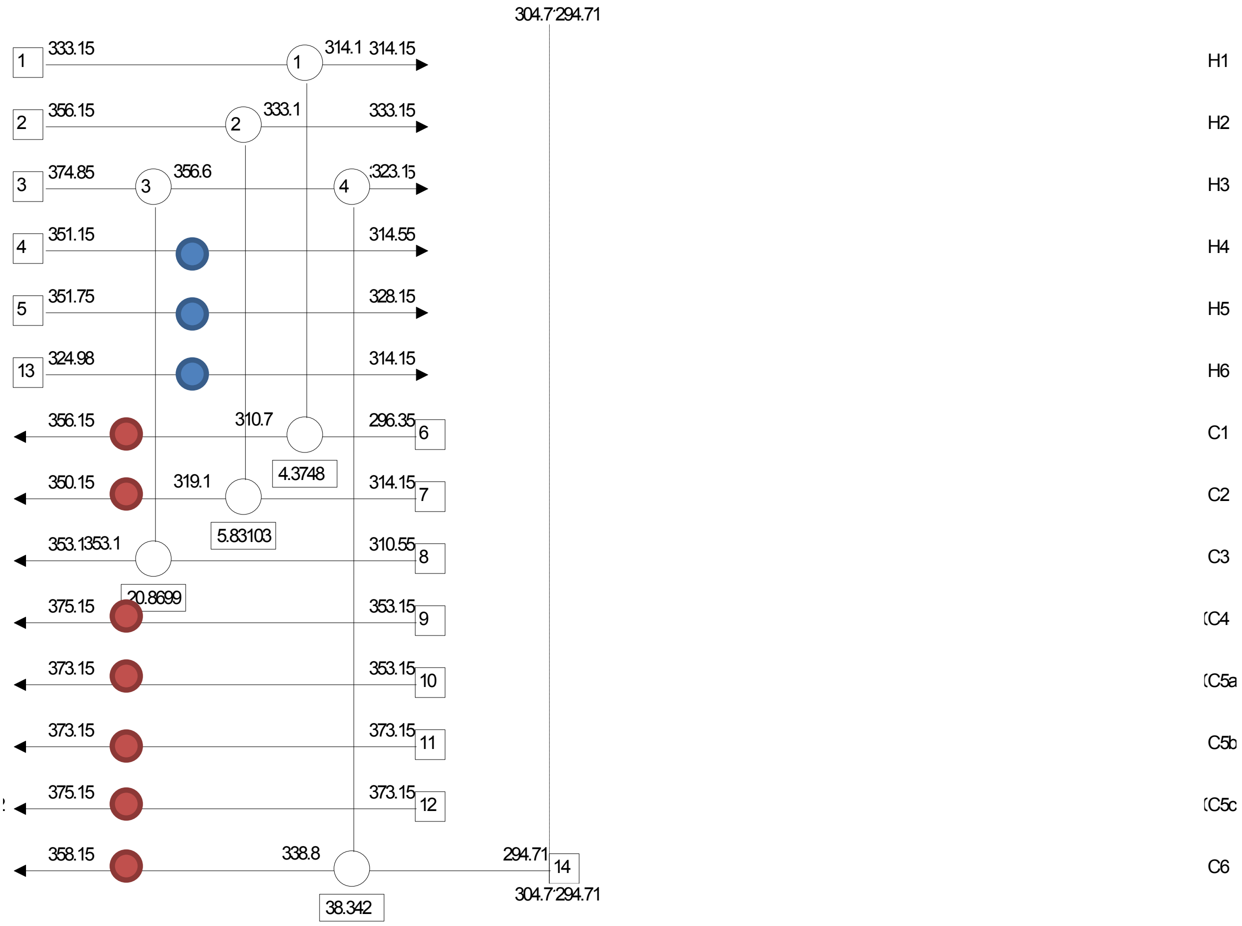

Figure 5.9: Grid diagram with streams, matches between process streams and utility matches for Process design 3

The other 10 units required are related to the satisfaction of the remaining heating demands of all the cold streams and the remaining cooling demands of all the hot streams by use of external utilities. However, streams C4, C5a, C5b and C5c above pinch constitute the protein dryer streams and may be counted as a single stream with one single match with external heating utility. Like that, the total number of units required for satisfaction of the streams considered in Pinch analysis becomes 11. However, one must also consider the streams of the process that are not included in Pinch analysis network in order to obtain a complete picture of the heat exchanger network and total external cooling and heating required by this Process design. These streams include the reboilers and condensers in distillation columns as well as the reactors, i.e. 8 heat exchanger units more. Thus the total number of exchanger units becomes 19 for this case.

ii. Pinch analysis with integration of condenser in the distillation column

As for Process design 2, once the pinch temperature is defined, integration of distillation columns and reactors may be discussed. The following tables summarize the decision-making process for integration of these units.

Table 5.12: Hot streams related to distillation columns and reactors

HOT STREAMS			
Unit	**Temperature (ºC)**	**Above or below the pinch**	**Interesting for Integration**
Fermentation (exothermic)	41	Below	No
Enzymatic hydrolysis (exothermic)	55	Above	Yes
Condenser in distillation column	81.52	Above	Yes
Condenser in rectifier	77.88	Above	Yes

Table 5.13: Cold streams related to distillation columns and reactors

COLD STREAMS			
Unit	**Temperature (ºC)**	**Above or below the pinch**	**Interesting for Integration**
Saccharification (endothermic)	60	Above	No
Lignocellulose pretreatment (endothermic)	85	Above	No
Reboiler in distillation column	101.85	Above	No
Reboiler in rectifier	83.87	Above	No

Firstly, the reactor for enzymatic hydrolysis of lignocellulose is an exothermic reactor placed in the temperature region of the Pinch analysis where there is heat deficit. Consequently, it is marked as interesting for integration. However, because of the complexity of reactor integration design and because of having a relatively very low duty, it is rare for any attempt to be made to recover heat from the reactor for such a case. Instead, utilities will be used. Thus, for system simplicity constraints, this option will not be contemplated in this study.

On the other hand, both condensers also operate above pinch, thus their integration in pinch analysis may be of interest since there is heat deficit in that region. The reboilers also lie above pinch, consequently being the columns not placed across the pinch.

As discussed for pinch analysis of Process design 2, integration of the condenser is limited by one of the constraints to achieving its complete cooling by using only *one* cold stream. This measure is adopted for design simplicity purposes. According to that, a cold stream with a heat duty equal or higher than the duty of the condenser is the only possibility for a match with this unit of the distillation column. As occurred already for Process design 2, the duties of both condensers are higher than any other duty among the cold streams in the system. For this reason, integration of distillation columns in this system does not seem a feasible improvement according to the constraints in the present plant design.

As a conclusion, the heat exchanger network proposed without integration of distillation columns shows to be the most appropriate for energy recovery in Process design 3.

Table 5.15 presents the required number of heat exchangers for the proposed HEN, as well as the proportion of the actual energy savings obtained by the proposed HEN compared to the potential energy savings in MER network design.

Table 5.14: Summary of key figures of proposed heat exchanger network for Process design 3

Proportion of actual energy savings obtained by the proposed HEN compared to the potential energy savings in MER network	70.08%
Number of matches between process streams	4
Total number of heat exchanger units	19

Chapter 6

Process Economics

Results on the total cost and revenues of each of the three Process designs in this study would lead to the ability to perform a trade-off between dextrose and starch-derived ethanol, and a trade-off between briquettes and lignocellulose-derived ethanol. According to the available information at the time of this study, a simplified economic assessment is performed in line with the results from the accomplished mass and energy balances.

6.1 Comments on Results from Simulations

As already stated in Sub-section 1.3 "*Goal of this study*", the results on mass balances by Aspen Plus are kept outside this report due to their confidentiality.

The following list aims to give a vision of the accomplished calculations and interesting results obtained by simulations on Aspen Plus in this study, even though the figures are not shown in this version of the report:

1) Product mass output of protein concentrate and its composition – same for Process design 1, 2 and 3.
2) Product mass output of briquettes and their composition for Process design 1 and 2.
3) Product mass output of dextrose/sugar and its composition/purity for Process design 1.
4) Product mass output of starch-derived ethanol and its purity for Process design 2.
5) Product mass output of starch- and lignocellulose-derived ethanol and its purity for Process design 3.
6) Product mass output of stillage from the distillation columns and their composition for Process design 2 and 3.
7) Heating and cooling requirements for each Process design.

All these results were used for the economic assessment, although only the scheme followed to do this evaluation is shown in this chapter provided that the results are confidential.

6.2 Economic Assessment

The total cost of the proposed Process designs has two main elements: capital cost and production & operating costs. The capital cost is determined partly by the plant design, equipment chosen, and installation cost. On the other hand, production & operating costs are associated with the day-to-day operation of the plant. Important production & operating costs are, for example, from raw materials and utilities.

By performing mass and energy balances on Aspen Plus, detailed information is provided for the production & operating expenses. However, enough information on capital cost was not available at the moment of this study and, thus, only the available production & operating costs are analysed. The lack of data due to the early phase of PoE project hinders this study on the ability to analyse the project for net profitability. The trade-off between the different products is hence performed by comparing the products revenues only with some of the production & operating expenses.

In general terms, the major factors affecting plant production & operating costs for the plants in the present study are the following fixed and variable costs: feedstock, labour, energy, enzymes, yeast, chemicals (e.g. nitric acid for lignocellulose pretreatment, anti-foaming chemicals, or chemicals for pH control), waste handling charges, and fixed charges (i.e. depreciation, licenses, maintenance, taxes and insurance). All these factors lead to the evidence that the costs of this type of biorefineries on a small scale can be extremely variable. A profitable operation requires a complete understanding of each of the variables affecting operating costs and the ability to keep these costs to a minimum. Furthermore, the ability to profitably sell or use the products is required as well (Gildred/Butterfield Limited Partnership, 1984).

Raw material quantities used and wastes produced were determined using the Aspen mass and energy balance model. Table 6.1 presents the costs of some of these items used for the economic assessment. In agreement with the accessible data, only the following variable costs are estimated: biomass feedstock, enzymes, yeast and organisms, and heating demand (electricity and cooling demands are a minor cost compared to heating demand).

Table 6.1: Variable Operating Costs for purchased items

Biomass feedstock	0.1369 €/kg DM ensilage
Enzymes (glucoamylase, alpha-amylase)	0.00735 €/L ethanol
Cellulase enzyme	0.021 €/L cellulosic ethanol
Yeast (*S. Cerevisiae*)	0.00209 €/L ethanol
Co-fermentation Organism (*Z. Mobilis*)	0.005461 €/L ethanol

Ensilage price is obtained from the report of the Proceedings of Forage Conference 2014, published by the Swedish University of Agricultural Sciences (Sveriges lantbruksuniversitet. Institutionen för växtproduktionsekologi, 2014). They based this figure on the prevailing prices in Sweden at the end of February 2013. Amylase enzyme and yeast costs for starch processing are obtained from a study by U.S. NREL (McAloon et al., 2000) which, in turn, got the costs from an industry source. The cost for the recombinant organism *Z. mobilis* is obtained from the same study, even if NREL assumes that the organism is grown on site, which was not included in the present study. It is thus recommended that better approximations are done for this cost in future studies by PoE. As for cellulase enzyme, its cost is also obtained from a study by NREL (Aden et al., 2002), which based this cost on purchased, delivered enzyme. All prices were converted to Euro for practical purposes.

As for the heating utilities, the briquettes may be considered to be used as a potential fuel source to meet the plant's own energy requirements. However, their direct sale as fuel to other industrial users or electricity generating companies is also attractive. As a consequence, two financial scenarios to evaluate the performance of the plant depending on the heating fuel are performed. In other words, the two scenarios represent a trade-off between selling the briquettes and using them as fuel for the own plant's heating demand.

Firstly, it will be assumed that the steam is generated by an industrial boiler run by wood chips with 70% efficiency (based on the assumptions for full load efficiency and continuous operation (Lantbrukarnas Riksförbund, 2011; International Energy Agency, 2010)). Secondly, the combination of self-produced briquettes and purchased wood chips will be considered for Process designs 1 and 2. In this second case, it is assumed that the installed wood chip boiler can also burn briquettes. Furthermore, it is also assumed that there is an improvement in the boiler efficiency due to the incorporation of briquettes, thus the boiler efficiency is set to 75%. Finally, for Process design 3 it is assumed that there is only one possible scenario where purchased wood chips are the unique fuel. Table 6.2 presents the cost of wood chips for purchase in the Swedish market, and the price of briquettes in the same market - at which the self-produced briquettes may be sold.

Table 6.2: Current cost in Sweden of the fuels considered for steam generation

	Wood chips	**Briquettes (self-produced)**
Cost/Price per unit of energy	0.02033 €/kWh*	0.02907 €/kWh*

**Source: Sveriges Officiella Statistik (2014)*

An estimation of the revenues from sales of the obtained products is also accomplished. Like that, another outcome of the economic assessment is the share of sales revenues by each product depending on the Process design, which will help PoE in managing market aspects for commercialization of the PoE technology. In this case, the eventual sales of the by-product fertiliser are not included due to lack of available data.

Table 6.3: Revenues Variable Operating Costs

Ethanol	0.6867 €/L ethanol
Protein concentrate	0.63826 €/ kg protein concentrate
Briquettes	0.13081 €/kg briquettes
Dextrose/sugar	0.3947 €/kg white sugar

Ethanol price is obtained from Börjesson et al. (2013). Protein concentrate price is obtained from the same source as ensilage cost (Sveriges lantbruksuniversitet. Institutionen för växtproduktionsekologi, 2014).

Briquettes price per unit of mass is calculated by using the Higher Heating Value (HHV) of briquettes (i.e. 4.5 kWh/kg) (Kalmarenergi AB, 2014) and the briquettes cost presented in Table 6.2. The source for sugar price is obtained from the European commission Portal (European Commission, 2014).

6.2.1 Process design 1

As Pinch analysis of Process design 1 is not performed for this study, calculations on gross profit for this process design are accomplished by making the assumption of no plant heat integration. Like that, the comparison of sales revenues with production & operating costs assumes the complete fulfilment of the plant's heating load by the on-site boiler (which burns different type of fuels depending on the scenario). The total heating demand of Process design 1 is obtained from the energy balances previously performed on Aspen Plus.

i. Biomass Heating System using Wood Chips

In these calculations, it is assumed that briquettes production is fully used for sales whereas wood chips are the fuel used to meet the heating requirements of the plant. In order to calculate the annual energy that must be delivered by wood chips, the annual total external heating required by the plant is divided by the boiler efficiency, i.e. 70% Once the need for wood chips fuel purchase (the amount of kWh per year) is defined, the total variable costs of the plant for Process design 1 are calculated by multiplying the individual costs of biomass feedstock, enzymes and wood chips by their annual demand. As for revenues calculation, the individual selling price of each product (i.e. dextrose, protein concentrate and briquettes) is multiplied by their annual production. Finally, by comparing the sales revenues with the annual production & operating costs, a first estimation of the gross profit of the plant is obtained.

ii. Biomass Heating System using Wood Chips and Briquettes

In this case, it is assumed that briquettes production is completely used on-site for steam generation in the plant, by burning in a 75%-efficient boiler. In order to calculate the remaining heating demand to be covered by wood chips, the following steps are followed:

1) The useful heat provided by briquettes is obtained by multiplying the annual production of briquettes by the boiler efficiency, i.e. 0.75.
2) The resulting figure for the useful heat provided by briquettes is subtracted to the total external heating required by the plant.
3) This remaining energy must be provided by the wood chips, thus this value is divided by 0.75 in order to get the annual required heating that must be contained in purchased wood chips.

With these calculations, the share of heating requirements that could be met by burning briquettes could also be provided as interesting informastion to PoE. Once the need for wood chips fuel purchase has been defined, the total variable costs of the plant for Process design 1 are calculated. The only difference with the previous case is the purchase of wood chips. On the other hand, in this case the revenues include only revenues from the products dextrose and protein concentrate. Finally, by comparing the sales revenues with the annual production & operating costs, a first estimation of the gross profit of the plant is obtained.

As a result, for Process design 1 the simulations and the aforementioned calculations on economic assessment clearly point to one of the scenarios as more economically feasible. However, this information is kept as confidential.

6.2.2 Process design 2

i. Biomass Heating System using Wood Chips

Calculations on the need for wood chips purchase are the same for this scenario as for the case of considering that briquettes are sold in Process design 1. Data on external heating demand required by the plant is obtained from Pinch analysis on Chapter 5. Once the need for wood chips fuel purchase has been defined, the total variable costs of the plant for Process design 2 are calculated. In this case, apart from biomass feedstock and enzymes, yeast is also added in the annual costs. The revenues of the product outputs for Process design 2 if briquettes are sold include ethanol, protein concentrate and briquettes sales. Finally, by comparing the sales revenues with the annual production & operating costs, a first estimation of the gross profit of the plant is obtained.

ii. Biomass Heating System using Wood Chips and Briquettes

The same steps for calculations on the need for wood chips purchase are followed for this scenario as for the case of considering that briquettes are burned on-site in Process design 1. Once the need for wood chips fuel purchase has been defined, the total variable costs of the plant for Process design 2 are calculated. The only difference with the scenario above is the purchase of wood chips. In this case, the revenues include only revenues from the products ethanol and protein concentrate. By comparing the sales revenues with the annual production & operating costs, a first estimation of the gross profit of the plant is obtained. For Process design 2, the simulations and the aforementioned calculations on economic assessment point to one of the two scenarios as more economically feasible. Furthermore, in terms of comparing Process design 1 and 2, the calculations provide information on which alternative is more economically feasible, thus on the trade-off between producing sugar or ethanol from the starch fraction.

6.2.3 Process design 3

In these calculations, burning wood chips fuel is considered as the only alternative to meet the heating demand of the plant. Thus, same calculations are done to find the need for wood chips purchase, and the total variable costs of the plant for Process design 3 are calculated. In this design, the variable costs include biomass feedstock, amylase enzymes, cellulose enzyme, fermenting organism *Z. Mobilis*, and wood chips. The annual revenues include sales of ethanol and protein concentrate.

As a conclusion of the results in Chapter 6, the alternative with the highest annual gross profit by only considering the available annual production & operating costs is obtained.

Chapter 7

Discussion

The purpose of this work was to create a model for each of the PoE plant configurations that calculates mass and energy balances and operates safely in Aspen Plus simulations, together with performing a heat integration analysis to observe the potential heat savings by exchanging heat between process streams.

When starting this work, the assignment was relatively open and there were not many restrictions in what should and should not be included in the model. Consequently, there was a lot of freedom to focus on the parts of interest. Because of the "commercial context" in which this thesis was performed, it was obvious from the beginning that a significant focus would be put on obtaining reliable data on the product mass flow outputs of the plant and on the energy use.

The first decision to take was on how to approach the plant-level modelling, since one may choose between a theoretical and an empirical approach. A theoretical approach will try to construct the model according to the laws of nature, by developing mass and energy balances for each process area, including detailed chemistry and physics for each unit. In an empirical model, on the other hand, available empirical data (i.e. inputs and outputs of individual process areas) is used to fit a regression equation or system of equations in each process area, and then all areas are linked to describe an entire plant (National Research Council of the National Academies, 2005). At the beginning, the intention was to use both the aforementioned approaches so that the model would be based on both theory and data.

First, examples of process units that were modelled with the theoretical approach are distillation columns or evaporators and dryers. However, as the work progressed, it became obvious that the data needed to use the empirical approach with some other units was in some cases not available, and neither was available the required detailed chemistry and physics for those same cases. Thus, the solution found was to fit empirical data from other studies found in the literature. These studies treated a similar feedstock and had the same goal as the unit operations in the present model. Examples of it are starch-protein separation in the decanter by means of adding the so-called “transfer solution”, and protein skimming by mechanical means.

The main effect of the lack of available data is that validating the model has been difficult. Thus, focus has instead been put on constructing a user-friendly model that operates in a robust way. It should, however, be stated that the model is in need of a thorough validation. Fortunately, such a validation is actually the next step in the plans on Peas on Earth project. PoE is planning to empirically validate the yields of the technology by collaborating with an existing testing facility for production of pilot quantities of new bioproducts. Therefore, the simulations in this study are valuable for PoE, since they allow knowing which process steps are critical in terms of product yield validation and where to put the strongest optimization efforts.

As for the heat integration analysis, results were also revealing since two of the heat exchangers in the proposed HEN had already been proposed by PoE before this study, although no detailed heat transfer analysis had been done until the moment. The present work revealed that further heating was required in order to warm the 2 cold streams in heat exchangers H1-C1 and H2-C2 up to target temperatures, since the corresponding hot streams did not have enough heat load. Moreover, new feasible matches between hot and cold streams were proposed in this study.

The economic assessment in Chapter 6 did not have a significant importance due to the lack of information on capital cost investment. Nevertheless, information on the shares of revenues income by each product was interesting in order to do a first rough evaluation of the trade-offs between starch-derived ethanol and dextrose, and between briquettes and lignocellulose-derived ethanol. But in any case, these trade-offs will only be completely reliable if capital costs are considered as well.

Hence, due to all the discussion presented in this chapter, it is recommended that this work is expanded by PoE to the areas that follow.

First, the collection in a testing facility of empirical data on the outputs of the most critical unit operations is recommended, i.e. on starch-protein separation in a decanter (while defining also if it will be a decanter by gravity or centrifuge), protein skimming by mechanical means, and lignocellulose-to-ethanol conversion.

Second, narrowing the Product Design Specifications according to real potential customers' requirements has been observed as key factor for more reliable simulations.

Third, specifications for each piece of equipment together with process equipment costing should be defined, in order to develop purchased equipment and installation costs. Equipment costs may be obtained from vendor quotations when possible, especially for uncommon equipment such as pretreatment reactors. NREL, for example, developed its own process engineering equipment database both for ethanol production from corn and from lignocellulose (Aden et al., 2002), with detailed specifications of design and cost estimation, thus this database could be used as a good first source for equipment specifications. Once the equipment costs are obtained, overhead and contingency factors may be applied to determine a total plant investment cost. That cost, along with the plant operating costs (mostly considered in this work with some exceptions, e.g. water consumption, cooling or electricity consumption) may be used in a discounted cash flow analysis to determine the production costs, using a set discount rate (Aden et al., 2002).

Fourth, effects of technical development on the energy demand may be examined. For example, in case of including ethanol production from lignocellulose, "Simultaneous saccharification and fermentation" may lead to better yields for ethanol production than the simulated "Separate hydrolysis and fermentation", as many studies on lignocellulosic ethanol have shown (Balat, 2011). Another example may be a new design consisting of an integrated distillation column with a fermentor, which could decrease the ethanol content in the fermentor stream and increase the ethanol content in inlet column stream. The new design would reduce the ethanol inhibition to yeast growth and save energy demand in the distillation section (Mei, 2006). These new designs could also be modelled on Aspen Plus.

Fifth, inclusion of wastewater treatment and combustor-boiler system in Aspen Plus simulations should be considered to have a complete view for plant integration purposes, as well as the recovery of valuable compounds from the residues of the plant.

Finally, it is also recommended to perform a study on the available renewable fuels that could be used for heating purposes depending on plant location, and on the environmental performance of the products from the present biorefinery with conventional products.

Chapter 8

Conclusions

This thesis has been performed in collaboration with Renetech AB, which has engaged in the development of the system aspect of Peas on Earth technology. Renetech was interested in obtaining detailed calculations on the product mass outputs, energy use, and opportunitites for heat integration of the PoE technology. The aim of the thesis was therefore to provide Renetech with this desired information. This was accomplished by building and describing a simulation model that calculates mass and energy balances of the overall biorefinery process on the simulation software Aspen Plus®. The simulated process converts the three fractions obtained from the ensilaged legumes into a variety of products, such as bioethanol fuel, protein for feed/food grades, dextrose to be sold as sweetener, and briquettes fuel, depending on the chosen plant configuration.

At the beginning of the work, the not-experienced user behavior resulted in time consuming problems with the simulations. But these problems were overcome after some time by learning from the committed errors. The resulting model constructed on Aspen Plus has demonstrated to be a robust tool for simulation and evaluation of complex processes like those involved in ethanol production, leading to thorough mass balances of every plant configuration. However, the lack of available empirical data on some specific unit operations (e.g. starch-protein separation in a decanter and protein skimming) was a significant drawback against obtaining a more correct and near-reality simulation of the operation units. Nevertheless, results on mass balances should be useful as information for economic evaluations, but also for comparison of the environmental performance of the products from the biorefinery with conventional products.

The model provides a considerably realistic basis for energy demand estimation and for economic analysis. The economic assessment gave results of the gross profit of each plant configuration, since information on capital cost was not available at the moment of this study. Also, one of the questions answered in this work was how much share of the heating requirements could be met by burning the lignocellulosic residues of the plant previosuly converted to briquettes. Moreover, a comparison of two scenarios for briquettes handling was done, that is, a scenario where briquettes are burned in the on-site boiler and a scenario where they are sold instead. The simulations and calculations on economic assessment clearly pointed to one of the alternatives as more economically feasible, among the three Process designs. Like that, a first trade-off could be done between sugar and ethanol from starch, and between briquettes and lignocellulose-derived ethanol.

Another outcome of the economic assessment in this study is the share of sales revenues by each product depending on the Process design, which will help PoE in managing market aspects for commercialization of the technology.

As for the energy balances by Aspen Plus, they showed that (for the cases where ethanol production is considered) condensers in the distillation columns are among the most energy-intensive hot streams and require most of the cooling load of the plant. Also, due to the vast mass flow of the stream entering distillation when lignocellulose-derived ethanol is also produced, the cooling demand of the stillage from the bottoms of the first distillation column is very high. On the other hand, the plant in general requires more heating than cooling load. Again, distillation columns represent some of the highest heating demands in their reboilers, together with the protein concentration dryer and (in case of lignocellulose-derived ethanol production) the heating of lignocellulose up to pretreatment temperature.

According to the results of these energy balances, a Pinch analysis was done with help of HINT software, which showed the opportunities for heat integration in the process. It must be remarked that this analysis involved many constraints in order to maintain the plant simplicity that PoE planned to include as an attractive feature of their technology. Consequently, the constraints lead to lower energy savings compared to the potential savings obtained when performing a pure Pinch analysis, i.e. results suggested that only 83% of the actual potential energy savings could be obtained by implementing the proposed HEN for Process design 2 (with 4 matches between process streams), and a 70% of the potential energy savings could be obtained for Process design 3. Both cases involved no heat integration of the distillation columns even if this case was evaluated since they act as main energy consumers, due to the complexity that this heat integration would involve. PoE had already planned some heat exchanger matches before this study, and the present work revealed new feasible matches between hot and cold streams that would act as a measure for saving further energy in the plant. These suggestions will be considered when developing more in detail the PoE technology.

As a final conclusion, the main challenges encountered during the work were connected with the initial gathering of data to be input in the simulation. Aspen Plus requires a vast quantity of parameters and properties of all components to make the overall designs in the study thermodynamically rigorous, thus finding them in the literature while there is no empirical part in the thesis work became a time-consuming task. Another difficulty in simulating the plant was in the assumptions to be made in the separation units due to lack of information on the specific separation techniques that PoE was planning to apply. For all these reasons, a further study on simulations of the plant is recommended, but only after having obtained more extense empirical data of the outcomes of the processes that this exact feedstock goes through in the proposed biorefinery.

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APPENDIX A – Parameters and thermodynamic properties for Aspen Plus

The parameters and thermodynamic properties of the compounds that were not readily available on Aspen Plus were obtained from a database developed by NREL, which is specificalized in biochemical processes. This database is called ASPEN PLUS INHSPCD, i.e. In-house Pure Component Database (Wooley & Putsche, 1996).

Compound name	**Formula in Aspen Plus**	**Normal state**
Starch	C6H10O5	Solid
Protein	CH0.1097O5.0594N0.3662S0.00278	Solid
Protsol (solubilized protein)	CH0.1097O5.0594N0.3662S0.00278	Liquid
Fiber	C6H10O5	Solid
Ash	CaO	Solid
Oil	C18H34O2	Liquid
Water	H2O	Liquid
Solunkn	C0.5HO0.5	Liquid
Glucose	C6H12O6	Liquid
Ethanol	C2H6O-2	Liquid
Carbon dioxide	CO2	Gas
Cellullose	C6H10O5	Solid
Hemicellullose	C5H8O4	Solid
Xylose	CH10O5	Liquid
Lignin	C10H13.9O1.3	Solid
Lignsol (solubilized lignin)	C10H13.9O1.3	Liquid
Furfural	C5H4O2	Liquid
HMF	C6H6O3	Liquid
Xylitol	C0.5HO0.5	Liquid

Table A1: Formulas for components used in the simulations, from Aspen Plus INHSPCD (NREL Biofuels) Databank

Assumptions for the simulations (same assumptions as the ones taken by McAloon et al. (2000)):

- Starch is considered to be a solid throughout the process and will never be in solution. Additionally, starch is a polymer, but its molecular weight formula will be taken as the repeat unit only.
- Glucose, although generally considered a solid at the temperatures involved in the ethanol process, is exclusively in aqueous solution. It will therefore be modeled as a liquid, although it will never exist as a pure liquid in the process.
- Protein is considered as completely dissolved, i.e. exclusively in aqueous solution. Therefore, it will be modeled as a liquid except for the streams after the coagulation tank.
- Solunkn is an unknown compound. It was given a reduced formula of xylose for material balances purpose only.

Liquid component	**MW**	**Tc (°C)**	**Pc (atm)**	**DHFORM (cal/mol)**	**RKTZRA (cum/kmol)**	**Vc (cum/kmol)**
Glucose	180.16	737.95	61.18924	-300407.02	0.35852	-
ProtSol	98.28	737.95	61.189	-182827.75	0.09908	0.4165
Oil	282.46	507.85	13.718	-1.52e+5	0.2377	-
Water	18.0152	373.98	217.666	-57756.28	0.243172	-
Ethanol	46.06	240.77	60.676	-56116.84	0.248507	-
CO2	44.00	31.06	72.86	-93988.24	0.2727	-
Solunkn	15.01	737.95	61.18924	-28441.68	0.09404	0.4165
Xylose	150.13	617.27	64.91685	-248570.74	0.29936	0.3425
LignSol	122.49	737.95	61.18924	-4.69e+5	0.35852	0.4165
HMF	126.11	457.86	51.6734	-77340.45	0.1982	0.3425
Xylitol	152.15	737.95	61.1892	-28422.66	0.09404	0.4165

Table A2: Values for liquid components in Aspen Plus INHSPCD Databank

Values for parameters to define PLXANT, CPIG and DHVLWT on the software were also obtained from NREL's INHSPCD Databank although they are not displayed in this Appendix.

Solid component	**MW**	**DHSFRM (J/kmol)**	**DGSFRM (cal/mol)**
Starch	162.1436	-976362000	-
Fiber	162.1436	-976362000	-
Ash	56.0774	-635968000.366	-1.44e+5
Protein	98.285	-764220000	-
Cellullose	164.1436	-976362000	
Hemicellullose	132.117	-762416000	
Lignin	122.493	-1592659000	

Table A3: Values for solid components in Aspen Plus INHSPCD Databank

Values for parameters to define CPSPO1 and VSPOLY on the software were also obtained from NREL's INHSPCD Databank although they are not displayed in this Appendix.

Appendix B – Material balances prior to simulation by Aspen Plus

According to the lab analyses of the sample, both moisture and protein contents of the biomass after ensiling are the following: 56% of moisture and 23.1% of protein on a dry basis. All the pieces of data obtained by lab analayses that are interesting for the material balances prior to simulations are listed as following:

- Annual input: 3500 tonnes DM biomass/year
- 44% of DM in input biomass
- 23.1% of DM in biomass is Protein
- 12.6% of DM in stalks is Protein
- 73.4% of DM in extract is Protein
- 25.7% of DM in beans is Protein

As for the moisture content in both the stalks and the extract fraction, reasonable assumptions are required due to lack of data:

- 40% of moisture in stalks fraction. Same assumption as in previous study by SLU on PoE lifecycle analysis (Karlsson et al., 2014).
- 6% of DM in the liquid extract fraction (Andersen & Kiel, 2000).

In order to calculate the mass flows of each of the three fractions obtained from the wet thresher, a further assumption is required:

- A 53.98% of DM in biomass follows the beans fraction - data for Faba bean by Jensen et al. (2010).

The goal of the calculations on material balances is to obtain the moisture content of the bean fraction, as well as the three mass flow rates entering the plant, i.e. mass flow rates of bean fraction, stalks fraction and liquid extract fraction. The annual wet biomass input is 7954.54 tonnes biomass/year. If the operating hours per year are 8400h, then the annual wet biomass input is 946.07 kg/h. The mass balances are the following:

1) Total mass balance:

$$946.97\ \text{kg/h} = \dot{m}_{stalk} + \dot{m}_{extr} + \dot{m}_{bean}$$

2) Mass balance on moisture content:

$$(1 - 0{,}44) \cdot 946.97\ \text{kg/h} = 0.4 \cdot \dot{m}_{stalk} + 0.94 \cdot \dot{m}_{extr} + M_{bean} \cdot \dot{m}_{bean}$$

3) Mass balance on "fraction of dry biomass following beans fraction":

$$0.5398 \cdot 0.44 \cdot 946.97 \text{ kg/h} = (1 - M_{bean}) \cdot \dot{m}_{bean}$$

4) Protein mass balance:

$$0.231 \cdot 0.44 \cdot 946.97 \text{ kg/h} = 0.126 \cdot 0.6 \cdot \dot{m}_{stalk} + 0.734 \cdot 0.06 \cdot \dot{m}_{extr} + 0.257 \cdot (1 - M_{bean}) \cdot \dot{m}_{bean}$$

Where $\dot{m}_{stalk}$ = mass flow of Stalks fraction (kg/h); $\dot{m}_{extr}$ = mass flow of liquid Extract fraction (kg/h); $\dot{m}_{bean}$= mass flow of Beans fraction (kg/h); and M_{bean} = moisture content of Beans fraction (decimal fraction).

The results of this equations system with 4 equations and 4 unknown variables are:

$\dot{m}_{stalk} = 280.42\ kg/h$

$\dot{m}_{bean} = 274.91\ kg/h$

$\dot{m}_{extr} = 391.64\ kg/h$

$M_{bean} = 18.19\%$

The result for beans moisture is close to typical moisture contents present in other studies (See example in Escribano et al. (1997)).