Dissertation

Polygeneration from Biomass -

Ethanol Production with Co-Generation of Electricity, Heat and Utilities in a Regional Setting

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Doktors der technischen Wissenschaften unter der Leitung von

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E 166
Institut für Verfahrenstechnik, Umwelttechnik und Technische Biowissenschaften der Technischen Universität Wien

eingereicht an der Technischen Universität Wien

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ABSTRACT

The transportation sector relies heavily on energy sources from fossil fuels that are threatened by resource depletion and responsible for global warming. Biodiesel, biogas and bioethanol among others have found consideration as renewable substitute. Large scale production of ethanol and biodiesel is burdened with a heavy penalty for fertilizers in industrial farming as well as transportation costs on the overall energy balance. Potential of valuable side products of farming such as wheat straw is left unused. In a small scale version of a ethanol plant fitting to a regional setting these shortcomings can be compensated for. To take advantage thereof the production facility design needs to be adapted. Large scale ethanol production relies on tailor made solution for a specific product. The process is highly integrated and efficient. The high investment costs in sophisticated detail solutions are compensated by the savings later in production.
This work is concerned with the design of a polygeneration process that is adapted to fit regional realities under the premise of energy efficiency and economic soundness. The evaluation is conducted for an ethanol production target of 1000 and 2500 t/a anhydrous ethanol. Wheat grain and straw, the major products of the model region north of Vienna, are the process substrates considered. Polygeneration allows the required flexibility in process design to accommodate the spectrum of substrates. By means of a design and selection phase four scenarios are chosen. Two of the process scenarios facilitate wheat grain, the other two wheat straw as substrate for ethanol production. The stillage is co-fermented with pretreated wheat straw in an anaerobic digester. To provide the steam utilities for the process the biogas is either burned in a combustion chamber or a gas engine. The latter yields electricity for self supply and the grid. The pretreatment of lignocellulose, residual biogas potential after ethanol fermentation of pretreated wheat straw and the heat integration of the process are analyzed in detail.
The grain based process with gas engine was found to yield the best performance. Wheat straw only schemes could not use the potential of lignin that makes up a significant share of the raw material. Although current as well as future scenarios such as pentose fermentation capabilities no polygeneration design was found that could produce at the going market rates of ethanol even with contribution from methane and electricity sales. Advances in pretreatment and enzyme technology have a large potential to improve the process. Lignin remains the key point to render straw-based processes competitive against grain. Future work should be focused on development of processing technologies for lignin.

KURZFASSUNG

Der Transportsektor ist derzeit stark abhängig von fossilen Energiequellen die innerhalb des nächsten Jahrhunderts erschöpft sein werden und zudem massiv zur globalen Erwärmung beitragen. Biodiesel, Biogas und Bioethanol -um nur einige zu nennen- aus erneuerbaren Quellen können Erdöl und Erdgas teilweise ersetzen. Die Energiebilanz von großindustrieller Biodiesel- und Ethanolproduktion wird belastet durch die Verwendung von Kunstdünger und den langen Transportwegen. Zusätzlich kann das Potential von wertvollen Nebenprodukten wie beispielsweise Stroh in solchen Anlagen nicht genutzt werden. In einer für regionale Gegebenheiten ausgelegten Bioethanolanlage können diese Nachteile ausgeglichen werden. Dafür ist jedoch das Anlagendesign spezifisch anzupassen.

Diese Dissertation beschäftigt sich mit dem Design eines Polygenerationsprozesses (Ethanol, Biogas, Dampf, Elekrizität, Wärme), dessen Rohstoffe ausschließlich regional bereitgestellt werden. Als Substrat für den Prozess wurden Weizenkorn und Weizenstroh in Betracht gezogen, die Hauptprodukte der Modelregion nördlich von Wien. Polygeneration erlaubt die benötigte Flexibilität im Prozessdesign, welche in Anbetracht der Heterogenität der Substrate nötig ist. Mittels eines Auswahlverfahrens wurden vier Prozesse festgelegt welche. Zwei der Prozesse verwenden Weizenkorn (Stärke), zwei weitere Prozesse Weizenstroh (Lignocellulose) als Substrat für die Ethanolproduktion. Der Fermentationsrückstand wird in allen vier Varianten nach der Destillation anaerob zu Biogas vergoren. Für die Produktion des Prozessdampfes wird das Biogas entweder in einem Kessel oder einem Gasmotor, welcher elektrische Energie für die Selbstversorgung, aber auch für das Netz, zur Verfügung stellt, verwertet. Die Vorbehandlung von Lignocellulose, die Abschätzung des verbleibenden Biogaspotentials nach der Ethanolfermentation von Stroh und die Wärmeintegration des Prozesses wurden in Studien untersucht. Der Ethanolprozess basierend auf Weizenkorn mit Co-Produktion von Elektrizität, Dampf und Fernwärme erwies sich als der Effizienteste. Prozesse die ausschließlich Weizenstroh verwerten, konnten den Ligninanteil des Rohmaterials nicht umsetzen und waren darum benachteiligt. Obwohl aktuelle als auch zukünftige Entwicklungen wie beispielsweise Pentosefermentation berücksichtigt wurden, konnte kein Szenario gefunden werden, welches zu den aktuellen Marktpreisen konkurrenzfähig ist. Jedoch haben sowohl die Strohvorbehandlung als auch die zu erwartenden spezifische Aktivitätszuwächse der Cellulasen ein großes Potential für Verbesserungen. Ligninverwertung bleibt der Schlüssel zu wirtschaftlichen Lignocelluloseprozessen.

LIST OF PUBLICATIONS

This thesis is based on the work published in the following articles:

I. Schausberger P., Bösch P., Friedl A. Modelling and Simulation of Coupled Ethanol and Biogas Production. *Clean Technologies and Environmental Policy Journal, In Press* **2009**.

II. Bösch P., Bauer A., Schausberger P., Amon T., Friedl A. A Novel Process Scheme for Selfsustaining Ethanol Production. *Proceedings of the 16th European Biomass Conference, Valencia, Spain* **2008**.

III. Bösch P., Wallberg O., Joelsson E., Galbe M., Zacchi G. Impact of 2 Stage Temperature Profile on Diluted Acid Hydrolysis of Spruce. *submitted to Biotechnology for Biofuels* **2009**.

IV. Bauer A., Bösch P., Friedl A., Amon T. Analysis of Methane Potentials of Steam Exploded Wheat Straw and Determination of Output Potentials of Combined Ethanol and Methane Production Yields. *Journal of Biotechnology* 142 {1}, **2009**, 50–55.

V. Bösch P., Schausberg P., Beckmann G., Jelemenský K., Friedl A. Example of Optimisation and Heat Integration on a Basis of Ethanol Plants. *Journal of Mechanical Engineering (Strojnícky časopis)* 59 {4}, **2009**, 205–215.

VI. Bösch P., Modarresi A., Friedl A. Exergy Analysis of Combined Ethanol and Biogas Polygeneration Plants. *submitted to Biomass & Bioenergy* **2009**.

Contribution by the author:

I. Responsible for simulation, data evaluation and writing.

II. Partially responsible for unit modeling and parameter collection.

III. Responsible for experimental work, data evaluation and writing.

IV. Responsible for experimental work, data evaluation and writing of the ethanol part.

V. I did basically all the work.

VI. I did basically all the work.

dolphins, no problem, ...

... skip this block for years.

un, deux, deux, deux, ...

ACKNOWLEDGMENT

The prime spot for acknowledgement is reserved for Prof. Anton Friedl without whom this sentence would never have been written.

Angela, who was always there.

Philipp, who was made to volunteer for the corrections, deserves special admiration and praise.

Maythee Saisriyoot, for having such a skillful lab partner was a great relief.

Christian and Markus, that provided me with all the resources required to complete my work.

The remaining colleagues at the VT Institute for creating a work atmosphere that is pleasant and stimulating at the same time.

The folks at the Kemicentrum, Lund, for making the trip to the north in the wintertime such a warm experience.

Besonderen Dank bin ich meiner kleinen aber feinen Familie schuldig.

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1

INTRODUCTION

The reliance on fossil fuels as energy source at the end of the first decade of the 21th century remains unchallenged. What has changed is the awareness of the population for the problematic aspects that come with this "addiction to oil" as the former president of the U.S.A. G.W. Bush Jr. had put it [1]. First there is considerable effort required to guarantee a secured supply of fossil energy which is crucial to sustain a stable economy. Second but certainly more fundamental is the issue of global warming caused by atmospheric enrichment of greenhouse gases such as carbon dioxide, methane, ozone and water vapor [2, 3]. The requirements for a sustainable solution can be summarized as:

- Carbon neutral (or negative)
- Renewable
- Produced domestically or within a reliable union
- Price levels equivalent to fossil fuel derived energy

Several pathways are taken to address these issues. Solar energy, wind energy, hydroelectric and geothermal energy and biofuels are considered to substitute fossil fuels. Another (although not renewable) energy source that is in its renaissance is nuclear power. The strategy of each nation to address the current situation is mainly given by its geographic and geologic realities. Countries with consistent wind patterns can rely on wind turbines to generate power. Solar power is best employed in areas with high levels of solar radiation. In mountainous countries like Austria or Norway hydroelectric power has long been exploited. Currently hydroelectric power is providing about 60% of the electric power or 9% of total gross energy consumed in Austria [4]. All schemes involving electricity work perfectly fine with stationary equipment but pose a significant engineering challenge when applied to the transport sector. This is due to the prevailing drawbacks of the current generation of accumulators (energy to weight ratio, recharge time, recharge cycles) to store that energy [5]. An alternative to all-electric vehicles is found with biofuels that can draw on the infrastructure already in place for gasoline and diesel engines.

1.1. Biofuels

Fuels derived from biomass are known by the term biofuels. The most prominent examples are bioethanol, biodiesel, biogas, biohydrogen. In contrast to fossil fuels can the substrates for biofuels be regrown within a human lifetime. In this context the prefix "bio" is used to indicate this aspect of these products. Depending on the production methodology of the substrate the term agri-ethanol and agri-diesel might also be found in the literature.

The European Commission acknowledges the following as biofuels [6]:

- **bioethanol**: ethanol produced from biomass and/or the biodegradable fraction of waste, to be used as biofuel
- **biodiesel**: a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel
- **biogas**: a fuel gas produced from biomass and/or from the biodegradable fraction of waste, that can be purified to natural gas quality, to be used as biofuel, or woodgas
- **biomethanol**: methanol produced from biomass, to be used as biofuel
- **biodimethylether**: dimethylether produced from biomass,to be used as biofuel
- **bio-ETBE** (ethyl-tertio-butyl-ether): ETBE produced on the basis of bioethanol. The percentage by volume of bio-ETBE that is calculated as biofuel is 47 %
- **bio-MTBE** (methyl-tertio-butyl-ether): a fuel produced on the basis of biomethanol. The percentage by volume of bio- MTBE that is calculated as biofuel is 36 %;
- **synthetic biofuels**: synthetic hydrocarbons or mixtures of synthetic hydrocarbons, which have been produced from biomass
- **biohydrogen**: hydrogen produced from biomass, and/or from the biodegradable fraction of waste, to be used as biofuel
- **pure vegetable oil**: oil produced from oil plants through pressing, extraction or comparable procedures, crude or refined but chemically unmodified, when compatible with the type of engines

The distinction of biofuels generations is frequently used in legal documents. The taxonomy allows the classification of substrates and processing methods:

- **First Generation Biofuels**
  Substrates for first generation biofuels are agricultural products with high starch content such as wheat or maize corn, sugar rich products like sugar beet or sugar cane that are all used for ethanol production and vegetable oils derived from oil

plants such as oil palm, sunflower or rapeseed used for biodiesel. The processes involved in the production have been known for considerable time as part of the food processing industry but are today optimized for maximal energy yield. A major drawback shared by all named substrates except sugar cane is the potential direct competition for acreage of high quality with food production. Depending on the substrates biogas and biohydrogen are considered part of this or the following category.

- **Second Generation Biofuels**
  Second generation biofuels are derived from agricultural and forest residues and from non-food crop feedstocks. Wheat straw and corn stover, bagasse from sugar cane production as well as rice straw are fine examples of residues. The total specific energy yield per acreage is considerably increased when using agricultural residues. Switchgrass and spruce can also be grown on land not suitable for the cultivation of crops. The substrates cannot be processed with standard equipment but require additional processing steps. In regard to technology the following definition is generally applicable for second generation biofuels [7]
  Biochemical - in which enzymes and micro-organisms are used to convert cellulose and hemicellulose components of the feedstocks to sugars prior to their fermentation
  Thermo-chemical - where pyrolysis/gasification technologies produce a synthesis gas (CO + H2) from which a wide range of long carbon chain biofuels, such as synthetic diesel or aviation fuel, can be reformed (Fischer-Tropsch process)

- **Third Generation Biofuels**
  This term is used as pool for very advanced processing technologies that yield biofuels but are a long time from industrial application. Second generation processes rely on conversion of lignocelluloses into monosaccharides by a pretreatment step followed by addition of an exogenously produced enzyme cocktail with or without simultaneous fermentation. Consolidated bioprocessing combines enzyme production, hydrolysis of cellulose and fermentation into one process step. To accomplish this advanced knowledge of the microorganism is required [8]. Another form of third generation biofuel is derived from algae that transforms solar energy directly into biodiesel passing on an agricultural derived intermediate.

Although the terminology strongly implies an advantage or benefit through the generations this cannot be generalized in this instance. For example a process scheme based on wheat grain that is fully integrated in terms of energy utilities can perform much better than a second generation based process that lacks fundamental engineering time.

1.2. Contemporary Ethanol Production

Today industrial ethanol is produced with first generation processes. Bioethanol from Brazil is mainly derived from sugar cane. U.S.A. and European ethanol is founded on starch rich grains (corn, wheat) as a source [9]. In 2008 the U.S.A. produced 26.9 Mt, Brazil 19.3 Mt and the E.U. 2.2 Mt (see Table 7.1). Every ethanol process relies on the same set of processes for fermentation and ethanol recovery. The fermentation can be operated either batch-wise or continuously. In general strains of the yeast *Saccharomyces cerevisiae* are used for ethanol production from hexoses. Acidity of the mash, temperature and alcohol levels have the biggest influence on the yield. Beers containing up to 16.5 wt% can be produced without slowing fermentation [10]. The beer is then distilled to yield an ethanol/water blend of around 94 wt% ethanol. The azeotropic point of the two components is at 95.6 wt% ethanol. The dehydration step is facilitated by a molecular sieve. The final product of anhydrous ethanol contains a maximum of 0.3 wt% water. The stillage of grain processes can be dried and sold as distillers grains. The major difference for various substrates is found in the preparation steps before the fermentation. Most straight forward is sugar cane that is milled and the juice clarified. The bagasse is burned to supply the process utilities. Grain is milled (wet or dry) followed by mashing, liquefaction and saccharification. The last two steps require enzymes that efficiently hydrolyze the starch to hexoses. The average capacity of ethanol plants built in the U.S.A. between 2006 to 2008 ranges from 120 to 390 kt/a [11]. The largest ethanol plant based on corn is operated by Jilin Fuel Ethanol Company, China with 585 kt/a [12]. Ultimately, ethanol production in large scale (>100 kt/a) from corn is efficient from an economic point of view since economy of scale effects lower the specific production price. However, the ecological value is still vigorously debated [13]. Undisputed is the necessity of first generation ethanol to establish the fundamental trading markets, the distribution and logistics network, in short the underlying industry.

1.3. Polygeneration

Following definition was used at the 1st European Conference on Polygeneration [14]:

The term "polygeneration" means an energy supply system, which delivers more than one form of energy to the final user, for example: electricity, heating and cooling can be delivered from one polygeneration plant. Polygeneration can involve combined co-generation (power and heat) or tri-generation (power, heat and cold) plants and/or district heating, preferably by renewable energy sources. Such polygeneration systems should be designed and controlled with a view to optimizing all relevant interactions between supply and demand. Their main benefit is in maximising the overall efficiency of the integrated system near the point of use.

The distinction to biorefineries lies in the fact that polygeneration provides energy where biorefineries supply ready chemicals or intermediates for further processing. Application of polygeneration on a system with biomass as primary substrate is found when a process produces electricity, district heat and solid/liquid/gaseous energy carriers. This is true for a broad spectrum of schemes from biomass incineration plants for electricity and heat to highly sophisticated systems with multiple products (oils, alcohols, methane, ...). The reasons for polygeneration in biofuel production are intertwined:

- Feedstock Composition: First generation biofuel processes rely heavily on feedstocks of high substrate quality. For example wheat grain is high on starch with amounts of proteins for distilled grains [15]. In contrats lignocellulose is considerably more complex in its composition with major contributions from cellulose, hemicellulose and lignin.

- Whole Plant Utilization: Wheat grain or maize corn represent only part of the biomass grown. The remaining straw poses an energy potential not yet utilized in large scale biofuel production.

- Process Economy: To enable efficient substrate utilization in the process the major components of the biomass have to be converted to the greatest extent (see item 1).

The principle of polygeneration was applied by Liebmann et al. for ethanol production [16]. The methodology used for life cycle analysis (LCA) was sustainable process index (SPI) that estimates the acreage required to completely embed a particular process into the ecosphere also reffered to as ecological footprint. The results shown in Figure 1.1 confirm that the ecological impact can be managed with this strategy. Where the ecological footprint of a traditional ethanol with DDGS production at 60 kt anhydrous ethanol is 55% of petrol, a plant that produces 1 kt per year of ethanol with a combined heat and power generation (CHP) requires only 8%. In other words the impact on nature is seven times smaller with a polygeneration plant of this setting. This was achieved by efficient acreage utilization through product diversification. For this work the denotation polygeneration is used in reference to a process that utilizes biomass to yield renewable energy in form of ethanol, biogas, electricity or district heat.

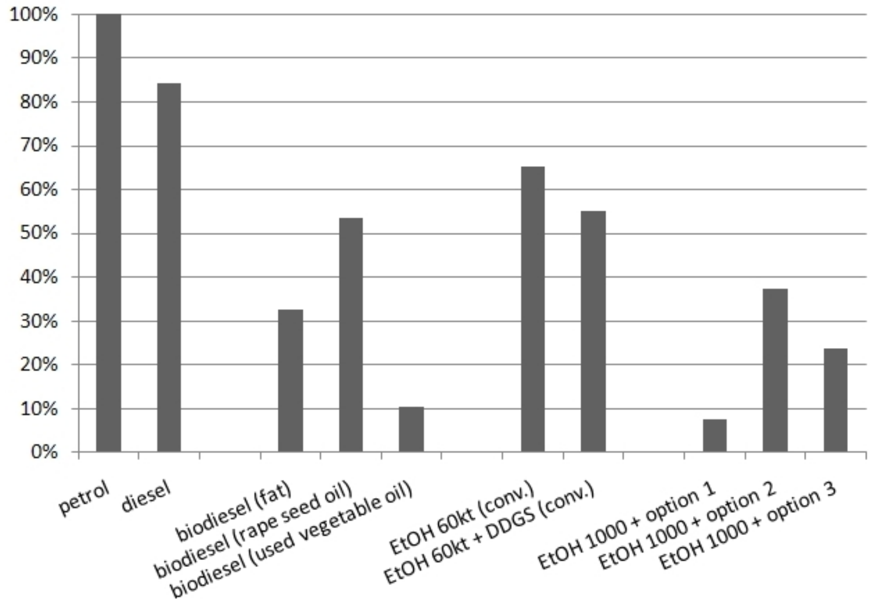


Figure 1.1: Ecological footprint of fossil and renewable fuels relative to petrol [16].
Option 1: biogas CHP stillage+straw+clover,
Option 2: biogas boiler stillage only,
Option 3: straw incineration

1.4. Aim and Outline of the Work

The conclusion from section 1.3 is that smaller, regional better integrated facilities have a lower ecological impact. As direct consequence thereof this thesis is concerned with the conception of a small scale polygeneration plant in Lower Austria. The main purpose of this work is the evaluation of polygeneration plants with lignocellulose as major substrate. The aim is to identify viable solutions in terms of ecology and economy to advance from first to second generation biofuels. The methodology is based on literature research, practical work, modeling and simulation, pinch analysis as well as investment calculation.

The proceeding Chapter 2 describes the legal framework and constraints for the project. Chapter 3 describes the selection process of polygeneration plants drawing from Paper I and II. A description of the engineering aspects in ethanol production can be found in Chapter 4 summarizing Paper III-V. Partly derived from Paper VI is Chapter 5 describing the process performance in regard to monetary and energy economy. Finally, some concluding remarks and suggestions for future work are given in Chapter 6.

2

LEGAL FRAMEWORK FOR POLYGENERATION

The task is not only defined by technical constraints but drawing from a historical background as well as a legal framework that has been highly dynamic in this decade. Therefore it is necessary to point out the external factors influencing the development of ethanol, electricity, biogas and district heat derived from renewable sources. Whenever possible the European consensus is reflected otherwise Austrian regulations will be described.

2.1. EU Policy and Directives

The EU strategy for biofuels is an essential part of the energy policy by the European commission. Under Directive 2003/30/EC a goal of 5.75% energy from renewable sources in the transport sector by 2010 within the EU was defined [6].
This was amended and subsequently repealed by Directive 2009/29/EC with a mandatory target of minimum 10% for the share of biofuels in transport petrol and diesel by 2020 which is part of a 20% overall Community energy consumption from renewables [17]. In the same paragraph the necessity to develop and fulfill effective sustainability criteria for biofuels in conjunction with the assessment of the possible impacts of biofuel production on agricultural food products is mentioned. Also the impact of indirect land-use change on greenhouse gas is addressed. No mandate to a specific biofuel is given. The member states can adopt these directives as they see it fit for their country. To promote the development within the member states several actions are taken [18]:

- Stimulating demand for biofuels
- Capturing environmental benefits
- Developing the production and distribution of biofuels
- Expanding feedstock supplies
- Enhancing trade opportunities
- Supporting developing countries
- Supporting research and development

Although measures are taken to meet the targets by 2010 is seems unlikely that the target is met according to "The Renewable Energy Progress Report" [19].

2.2. Ethanol

Ethanol is a substance with a very long tradition. These traditions are reflected in the laws and regulations concerning its utilization as chemical raw material, ingredient of beverages or recently in Europe as fuel.

2.2.1 Standards

For reasons of quality assurance, interoperability, trade and safety among others a standardization process was initiated by the EU. This should facilitate an efficient European market for fuel ethanol. The standard for fuel ethanol in the EU has the denomination EN 15376. The specifications can be found in Table 7.3. The maximal allowed water content is 0.3 wt% , the minimal required ethanol content 98.7 wt% . Is can be blended with gasoline according to EN 228 with up to 5.0 vol% (4.0 wt%) to yield E5.

LLE Ethanol-Water-Gasoline

The wet distribution system for gasoline across Europe requires low water concentrations in the standard to avoid phase separation that would lead to a diminished engine performance. The liquid-liquid-equilibrium (LLE) shown in Figure 2.1 demonstrates the difficulty. With blends of low concentrations even relatively small amounts of water lead to phase separation. Since the density of water is higher than gasoline or ethanol, water will always collect at the bottom of the tank or pipeline where generally the suction pipe is located causing ignition problems. Blends with an increased ethanol share (E10) allow for a higher water concentration. This will be a point of discussion in the next section. Other parameters affecting the miscibility are the temperature of the blend and the aromatic content of the base gasoline.

Convergence of national standards

Since Europe is a net importer of ethanol there is a strong incentive to have international valid standards for fuel ethanol [21]. In contrast to the Brazilian standard is the EN 15736 comparatively young. It was first drafted (prEN 15736) in conjunction with a taskforce involving Brazil and the U.S.A.. They concluded with the publication of a whitepaper that analyzes the major differences and the potential for convergence [22]. A list of national standards for fuel ethanol is compiled in Table 7.3 for Brazil, EU and

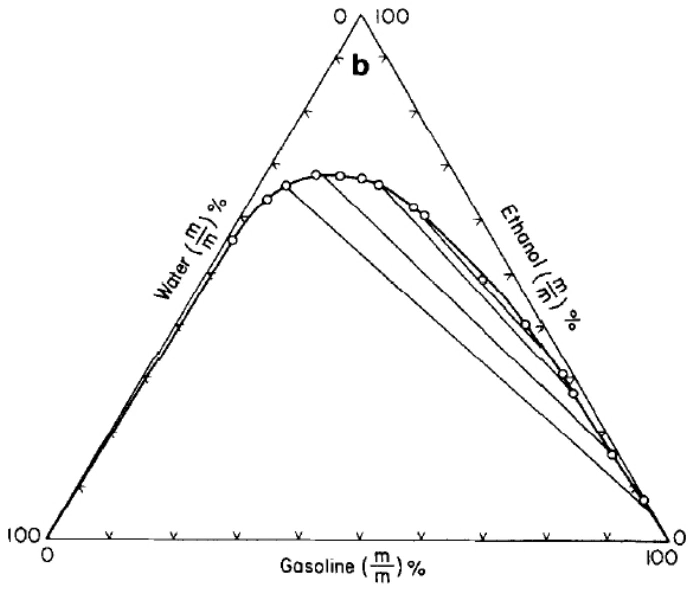


Figure 2.1: LLE Ethanol-Water-Gasoline [20]

U.S.A.. Table 2.1 shows the distinction of the properties into groups according to their similarities across the standards. Almost all parameters were similar or with significant differences but within reach of a compromise. The one sole fundamental difference was the water content. The ethanol content in the U.S.A. and Brazil is considerably higher therefore avoiding the phase separation problem to a great extent. Imports into Europe with the most stringent requirements on water content can be facilitated by additional drying by Brazil and U.S.A. exporters.

Table 2.1: Classification of Bioethanol Specifications by Similarity [23]

Category A	similar	color, appearance, density, sulfate content, sulfur content, copper content, iron content, sodium content, electrolytic conductivity
Category B	significant differences	ethanol content, acidity, phosphorus content, pHe, gum / evaporation residue, chloride content
Category C	fundamental differences	water content

2.2.2 Trade Barriers

Import Duty

The import duty of ethanol into the EU (third country duty) is for undenatured ethyl alcohol of an alcoholic strength by volume of 80 vol% or higher 19.20 €/hl (TARIC 2207 10) and for ethyl alcohol and other spirits, denatured, of any strength 10.20 €/hl (TARIC 2207 20) [24].

Subsidies

Since for most biofuels biomass for the conversion processes is the major cost factor subsidies have a direct and significant impact on the sales price of the product. E.g. in 2007 the EU turned into a net importer for methyl ester. Cause for this was partly cheap soy oil methyl ester from the U.S.A. which benefited from subsidies that undercut the prices and even the costs of European production. After an investigation the European Commission imposed provisional anti-dumping duties and countervailing duties [19].

Non-Tariff Barriers to Trade

Standards With limits preferring a specific production method and/or substrate a trade barrier can be put in place. This becomes apparent when discussing the specifications of fuel ethanol in regard to water content where the EU is importer with the highest demands on ethanol quality not matched by the exporters industries.

Denaturants To render alcoholic spiritis undrinkable they are blended with denaturants. Thereby no excise tax is due on this spirits. The excise tax amounts to 1000 €/hl in Austria. De facto every European country has its own requirement for denaturants [25]. A strong recommendation is given in EN 15376 for the following denaturants since no side effects for motors are known:

- gasoline according to EN228
- ethyl tert-butyl ether (ETBE)
- methyl tert-butyl ether (MTBE)
- tertiary butyl alcohol (TBA)
- isobutanol
- isopropanol

Every member state of the EU has accepted the others' state regulations concerning denaturation thereby allowing unrestricted trade [26]. If neither of the denaturation requirements are fulfilled the excise tax will apply. In Austria the following blend is applied: Per hectoliter of ethyl alcohol: 0,5 kilogram of fusel oil (by-product of alcohol rectification), 0,05 kilogram of gas oil from CN code 2710 and 1 kilogram of methylethylketone.

2.3. Biogas, Electricity and District Heat

Ethanol can easily be transported over great distances. In contrast to that biogas, electricity and heat are almost always tied to a distribution grid. The national and regional regulations have therefore a much more significant influence on the welfare of the industry.

2.3.1 Biogas

The composition of the gas stream after anaerobic digestion varies between 45-70 mol% methane, 30-45 mol% carbon dioxide, <5 mol% nitrogen and <2000 mg/m^3(STP) hydrogen sulphide. According to Austrian standard OEVGW G31 a maximum of 2.0 mol% carbon dioxide with traces of <5 mg/m^3(STP) hydrogen sulphide are allowed for gas in the natural gas grid. It is complemented by Austrian standard OEVGW G33 that requires a minimum of 97 mol% of methane. Hence an upgrading of the biogas is necessary to fulfill the requirements.
Common processes for carbon dioxid removal are pressure swing adsorption and high pressure water scrubbing. Another very promising option is gas permeation facilitated by a CO_2 selective membrane. A fully functional demonstration plant with a live feed into the natural gas grid is operating in Bruck a.d. Leitha, Lower Austria [27]. At the time of writing no standard rates for supplying the grid with biogas were put in place for Austria. An alternative to introducing the methane into the natural gas grid or power vehicles is utilizing it onsite by generating electric power and heat.

2.3.2 Electricity and District Heat

To be eligible for "ecological electricity" rates (Ökostrom) under Austrian law CHP's (Combined Heat and Power) with biogas require a raw material utilization degree of at least 60% [28]. The electric efficiency achieved by a gas engine is about 40%. The remainder is provided by the off-heat utilization powering a network of district heat as an example. The rates are degressive with increasing engine power (see Table 2.2). They are reviewed periodically by E-Control according to the development of the EEX base load quarterly future (Phelix) and published on their homepage [29]. Also the electricity

Table 2.2: Electricity from Renewable Sources, Rates for Biogas from Agricultural Products (Maize, Manure)

kW	c€/kWh
< 100	16.93
100 - 250	15.13
250-500	13.98
500-1000	12.38
> 1000	11.28

network operators are obliged to treat the companies seeking connection in a fair and transparent manner (”Anschlusspflicht”, [28]).

3

POLYGENERATION CONCEPTS

Based on the given legal considerations this chapter will explore the possibilities of process design in regard to regional characteristics.

3.1. Project Setting

Harmansdorf-Rückersdorf is the site the process is planned for. It is part of a rural area in Lower Austria 50 km north of Vienna. The focus of the proposed scenarios is put on small scale ethanol plants to sustain the local character rendering the population more independent, self supplying the community, preserving the farmland and creating jobs at the countryside. The process should utilize the full spectrum of the typical local agricultural products with the prevailing crop rotation cycle in a sustainable but efficient way. This becomes possible since the short supply distances allow the facilitation of otherwise low value agricultural residues such as straws. In 2007 the district Korneuburg - the mentioned municipality is part of which - produced in 2007 on 25669 ha cereals with a share of 14319 ha wheat grain, 5365 ha spring barley and 3695 ha of maize [30]. The integration of a small industrial park or the public buildings via district heat is potentially given and should be reflected in the decision process.

3.2. Process Simulation - Paper I

Although general calculations based on experience and approximations can give valuable insight into specific scenarios a more detailed and extensive analysis was required at this stage. To manage the multitude of scenarios without losing important particularities process simulation is used to fulfill the prerequisite. The major advantages of process simulation in this case are the fast processing of different scenarios and sensitivity analysis.
A suitable tool to accomplish this task is IPSE Pro. It therefore was extended by a library for ethanol production [31].To match the requirements for simulation of polygeneration plants the library was considerably enhanced in all regards providing better flexibility with more unit operations available such as biogas fermentation or steam pre-

treatment among many others. Paper I gives a detailed description of the fundamental modeling techniques in conjunction with the assumptions that are required. The parameters required for the models are either derived from literature, based on experiments and calculations or in some special cases from personal communication with partners from the industry.

3.3. Process Scenarios

To identify the most suitable process for the region a list of all feasible process units is created. By multiple stages of selection throughout the thesis the choices are narrowed down to the most promising solutions. An important aspect of the process definition are the substrates. They are system inherent to the region and are considered to be with limited flexibility.

3.3.1 Substrates

First the available substrates in the region are defined. Depending on the climate and the soil a variety of substrates qualify for ethanol production and/or cogeneration. The substrates considered in this work are summarized in Table 3.1. It gives an overview of agricultural products/residues that are grown in lower Austria.

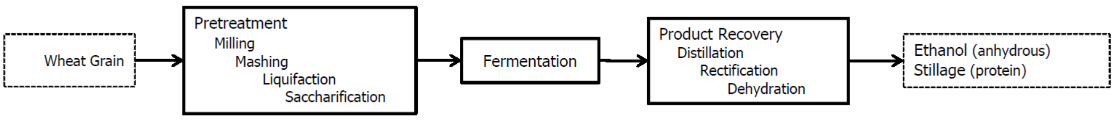
Table 3.1: Substrates for Polygeneration Processes

Substrates		Ethanol 1stGeneration	Ethanol 2ndGeneration	Biogas
Wheat	Whole Plant	-	+	+
	Grain	+		
Barley	Whole Plant	-	+	+
	Grain	+		
Triticale	Whole Plant	-	+	++
	Grain	+		
Straw		-	+	+
Maize	CornCobMix	+	+	+
	Corn	++		+
	Corn Stover	-	+	+
	Silage	-	-	++
Sudan Grass		-	+	+
Sunflower		-	+	+
Manure	Cattle	-	-	+
	Pig	-	-	+
Stillage		-	-	+

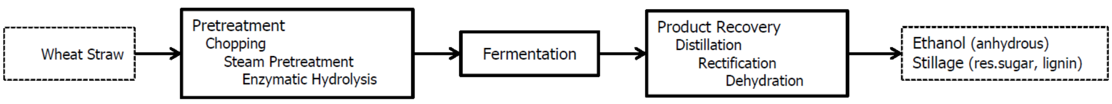
3.3.2 Processing Units

The polygeneration scheme is broken down into processing units. This approach is advantageous due to the reduced complexity of the later selection process. These "building blocks" of the process are partly standard processes that are well understood but also emerging ones that are still in development.

Starch-based Ethanol: The traditional way to produce ethanol was already introduced in section 1.2. The process is reliable, robust and can handle different starchy substrates. The high final ethanol concentration is a major asset since considerable energy reduction is achieved thereby increasing the overall energy yield. Since grain is almost homogeneous in its composition with 75.6 wt% starch per kg dry matter (DM) for wheat grain and 72.0 wt% for maize corn it is ideal to process since no fractionation of other constituents is required [15, 32]. Several points remain to be discussed for small scale applications since not every engineering solution for large scale can be applied to the smaller facilities. Especially the complexity of the product recovery part has to be reduced a great deal.



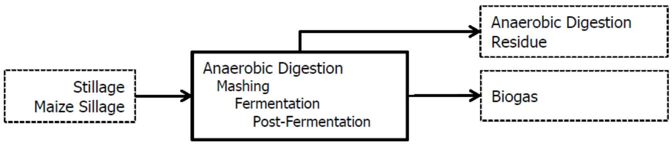
Lignocellulose-based Ethanol: Since this process is still in the demonstration phase several options have to be considered. The pretreatment method and its implication on the fermentation process, the hydrolysis step to yield the monosaccharides, the strategy for the fermentation process as well as the downstream that has to deal with low ethanol concentrations. Lignocellulose's major components are cellulose, hemicellulose and lignin. The latter is not suitable for ethanol fermentation reducing the specific yield per kg input. Since the process is not proven in industrial application an operational risk remains.



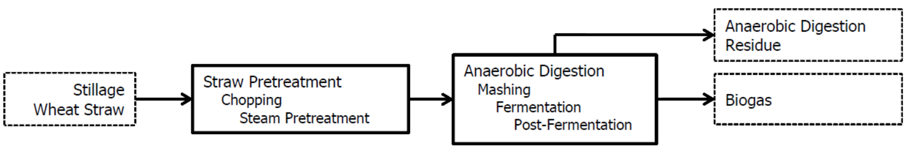
Distillers Grains: A byproduct of ethanol from starch is distillers grain, the dried residue of the fermentation stillage. With maize corn as substrate distillers dried grain (without soluble) are reported to contain 49.7 wt% neutral detergent fiber and 28.4

wt% proteins per kg DM with a remainder of fat, ash, organics and 9.0 wt% moisture [32]. The protein content is dependent on the cereal type and the quality. E.g. wheat grain contains 15.3 wt% of protein per kg DM ([15]) yielding a more valuable product in theory. The vending of distillers grain is a major revenue stream for starch based ethanol plants supplying the livestock industry.

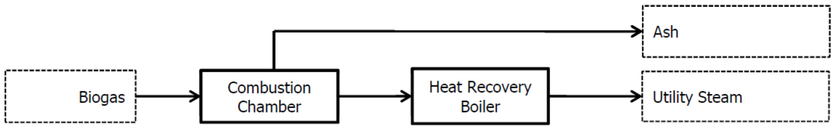
Anaerobic Digestion of Stillage and Maize Silage: The anaerobic digestion of maize silage is common practice. The silage is fed into a stirred fermentation vessel. The digestion is facilitated by a mixed culture of microorganisms that convert the substrate into carbondioxid and methane at anaerobic conditions. This broth can be supplemented with the stillage from the ethanol fermentation process. The gas phase rich on methane is sometimes further processed in a H2S scrubber to yield the product stream for further processing. The anaerobic digestion residue is returned to the field.



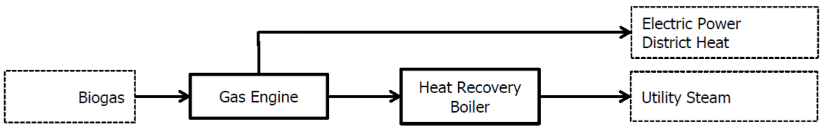
Anaerobic Digestion of Stillage and Wheat Straw: Unlike maize silage wheat straw cannot be directly fed into the fermenter for biogas production. Straw has a low density due to the air filled compartments. In the fermenter a layer of floating substrate would form resulting in an unacceptable space time yield. A solution to this problem is the processing of the straw with a pretreatment unit prior to the introduction into the fermenter. This facilitates a wetting of the plants structural cells in conjunction with an increased surface. The pretreatment reduces the holdup time in the fermenter significantly. The procedure comes at the cost of increased energy requirements. The stillage can be introduced to the straw either before or after the pretreatment.



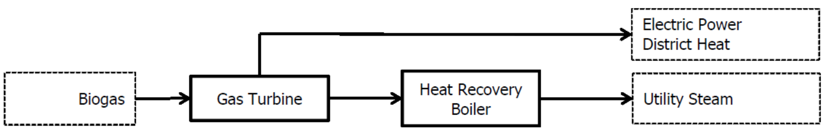
Utilization of Biogas in a Combustion Chamber: The most straight forward way to utilize biogas is by burning it in a combustion chamber. The heat of combustion is transferred via heat exchangers to a steam cycle that provides the remaining process with utility steam. The amount of biogas input (size of the fermenter) is set by the steam requirement of the process.



Utilization of Biogas in a Gas Engine: The most common form of biogas utilization in Austria is generation of electric energy with a gas engine. Beside electricity utility steam can be produced from the off heat in form of flue gas and the engines cooling cycles. This process is commonly refered to as CHP. The maximum in terms of electricity output is reached at around 5 MW per unit. The electric efficiency of these aggregates is around 41 %. The thermal efficiency that is about 43 % contributes to meet the regulations thereby qualifying for the higher rates (see 2.3.2).



Utilization of Biogas in a Turbine: With increasing demand of utility steam a shift from electric energy to heat can be a necessity. Gas engines have a fix ratio of eletricity to thermal output. For turbines this ratio can be modified by means of process design. This allows for a higher flexibility when dealing with heat integration of the process. Since the application of turbines in conjunction with biogas is not routine the suitability has to be clarified in terms of emission standards and efficiency.



3.4. Process Evaluation - Paper II

This section is concerned with the general performance of the introduced process units. The assessment highlights properties in regard to ecology, substrate utilization, process, engineering and costs. The evaluation is the basis for the later definition of scenarios.

Earlier project findings resulted in the following base assumptions for the decision process. The capacity of the ethanol process is set for a 1000 and 2500 t/a anhydrous ethanol target [33, 34]. Power generating units should be able to provide 700 respectively 1400 kW of electricity to the public grid as well as covering the self supply.

Starch-based Ethanol: Cultivation methods have a considerable influence on the ecological impact of farming [34]. With crop rotation strategies the need for fertilizers can be reduced and the overall soil quality improved. These methods will not yield the maximal output per area and year but ensure a sustainable cultivation. Maximized production of cereals does burden the overall LCA of the ethanol process. When limiting the analysis of the starch based ethanol to grain a high degree of raw material utilization is achieved. This view neglects that a good share of the biomass remains on the field unutilized. The defined ethanol production target requires an adoption of the standard fuel ethanol process. The production of yeast in the process is not economical for this size, neither is the recovery of yeast after the fermentation. The downstream part needs to be reduced in complexity thereby losing some of the energy efficiency. This becomes necessary since a large scale process can justify larger investment costs to recover them later by reducing the costs of operation. Also the dehydration step requires consideration since molecular sieve technology with a high degree of automation may not be cost efficient in contrast to a membrane solution. Apart from the modifications the process is well known and comparatively cheap. Besides ethanol the unit yields stillage, a process stream of high value.

Lignocellulose-based Ethanol: A major asset of lignocellulose-based ethanol production is the conversion of a low value agricultural residue in a valuable commodity. Thereby the overall yield per area is increased since the product spectrum is no longer limited to grain. The issue of soil depletion can be addressed by the measures introduced in the former paragraph. The ethanol process itself utilizes only part of the raw material. Depending on the fermentation technology only hexoses or hexoses and pentoses are converted to ethanol. Lignin with an approximate share of 1/5 per kg straw DM remains inert. Key elements of the process such as raw material pretreatment, hydrolysis and fermentation are still in laboratory or demonstration stage. Integration of pretreatment procedures is required to reduce the amount of consumed energy. The downstream is not only affected by the reduction in size but also by the reduction of ethanol concentration in the beer. As mentioned earlier beers in a starch-based process can attain 16.5 wt% beers derived from lignocellulose fermentation are aiming for 4-5 wt% [35]. The current prices for operational resources such as enzymes and yeast will weight down on the costs additionally to the engineering time. If these costs are compensated for by the cheaper raw material remains to be clarified.

Distillers Grains: Due to the low protein content of the stillage from lignocellulose distillers grains production is not applicable. However, for ethanol from cereals it is the standard procedure of disposal by creating an additional value stream. Therefore the technology is proven and applicable. A major drawback of the distillers grains process is the significant energy consumption. 53.5 % of total thermal and 41 % of total electric energy consumed by a standard ethanol process is utilized for evaporation and drying [10]. This puts a considerable penalty on the otherwise valuable product. A major concern is the downsizing of the utilities. With smaller equipment the efficiency of the process drops further. Especially the possibilities for heat integration with the distillation/rectification process are reduces in comparison to the large scale process. Also the specific cost for the equipment will increase severely.

The dried product is of high value as fodder for livestock since it is rich on proteins facilitating muscle buildup. There exist several different types of distillers grains depending on the processing procedure. Varieties with higher water content would reduce the utilities required for production but would also diminish the life span of the product. This would be an option with livestock farmers close to the facility.

Dry corn fractionation to recover germ and fiber prior to fermentation could be a option to produce a valuable product and decreasing the utilities required for distillers grains production [36]. Again the size of the operation makes this measure appear unlikely to be profitable.

Taking into account the given statements it is unlikely that the drying of stillage is viable under these general conditions since the production targets are to small and/or the purchasers for the commodity are too rare in the region. Therefore this process is not part of the considered polygeneartion schemes. Distillers grains production is not completely excluded from the evaluation process. It is part of the reference case in the later presented study on exergy.

Anaerobic Digestion of Stillage and Maize Silage: Maize silage is produced by fermenting the whole maize plant at anaerobic conditions. Thereby the integrity of the fiber is broken down. For the silage process a pit is required. It has to fulfill the specifications especially in regard to ground water protection since contaminating substances are formed during the fermentation. The silage is then fed into the anaerobic fermentation vessel were it remains 60-70 days [37]. The residence time of the substrate defines the size of the fermenter. Anaerobic digestion is common practice with years of experience building and operating the facilities. The size of one fermenter is limited to a diameter of around 35 meters. The costs for construction are considerable. The vessels including a stirrer for agitation and the groundwork including the sealing of the work area require massive investments. The amortization of these projects is generally in the range of a decade. Once the anaerobic digestion is complete the residue will be returned to the field providing fertilization and hydration. The high water content makes anaerobic digestion residue unsuitable for longer transport distances. The cofermentation of multiple substrates is possible since the anaerobic digestion is not facilitated by a specialized organism but by a mixed culture. The DM content in the vessel should not increase above 12 wt% since otherwise the agitation will not be thorough and zones of no activity will form reducing the performance. The provision of the maize will require setting aside arable land for the production.

Anaerobic Digestion of Stillage and Wheat Straw: The utilization of wheat straw via anaerobic digestion is by far not as challenging as ethanol fermentation. The pretreatment process doesn't require being as sophisticated and thorough. This is for two reasons. First, the residence time is a lot longer than with ethanol fermentation making a slower breakdown of the material acceptable. Second the fermentation is not as specialized with the mixed culture being better suited for the heterogeneous character of the substrate. The risks taken with implementing pretreatment processes are manageable. The size limitation of the fermentation vessels is not as pressing as in the case of maize silage since the holdup time - around 20 days - is considerably shorter (this was established in an experiment not disclosed in this thesis). This could potentially balance the higher investment costs of the pretreatment equipment.
Straw is available in abundance in the region considered. The price is likely to rise once a demand is created for by the process. This has to be kept in mind during costing. The utilization of wheat straw is not complete after anaerobic digestion. The lignin remains in the residue along with ash. The residue is not suitable for incineration since the ash content and composition result in a low melting point. This is already an issue when

burning native wheat straw.
Summarizing the consideration from the last two paragraphs in conjunctions with the conclusions drawn in Paper II leads to the elimination of the option "Anaerobic Digestion of Stillage and Maize Silage".

Utilization of Biogas in a Combustion Chamber: Biogas combustion cannot satisfy the facilities total energy demand since electricity for pumps, cooling utilities and automation is additionally required. But then cogeneration of energy will require more biomass input for example in form of maize silage. This will increase the fermenter size reflecting in investment and operation costs. Poorly operated fermentation could lead to low quality biogas that is not suitable for combustion. This has to be monitored to avoid unacceptable emissions. Apart from that is the process robust and affordable.

Utilization of Biogas in a Gas Engine: The range of available gas engines is conveniently overlapping with the defined requirements in terms of engine power (700 / 1400 kW). Engines of the required size come with two cooling stages. The high temperature cooling stage is suitable for powering a network of district heat. The off heat drives a boiler that is generating utility steam. A major drawback of gas engines is the fixed ratio of electric and thermal energy. In case the off heat generated by the gas engine is insufficient to cover the facilities steam demand a supplementary combustion chamber can be installed to provide the extra heat. This setup would require an additional boiler or at least separated heat exchanger area in the boiler for the flue gas. This is a measure required for the engines safety because at a standstill or malfunction the combustion chambers off gas would flow back into the engine over the shared piping risking corrosion. As intrinsic for Carnot cycles the electric efficiency is limited but the overall energy put into the engine is exploited well given the heat is also salvaged. The investment costs are considerable but design options like execution in containers in conjunction with the guaranteed feed in rates for electric power limit the uncertainties.

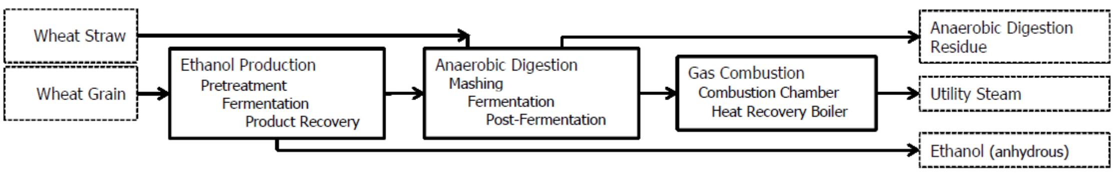
Utilization of Biogas in a Turbine: Unlike the situation with gas engines the choice of turbines in the considered range is very limited. No aggregates of the required size could be found. The smallest industrial size turbines deliver 1.5 MW electricity. Microgasturbines by Capstone and Bowman Powers of 80 kW electric output and Turbec of 100 kW electric output were available. To achieve the required power level six to eight aggregates have to be put in place. This would drive up investment costs to an unacceptable level not to mention the maintenance costs. In this form of execution the

system would be redundant to a high degree safeguarding against major outages. A asset of turbines over gas engines is that the electric power can be shifted in favor of the thermal output by means of the recuperator setting for some turbines (Bowman Powers). Since the composition of biogas is different to standard gas from fossil sources the suitability in regard to long term operation has to be checked. This becomes necessary because turbines are rarely used for this application.
In conclusion the turbine option will be dropped from further investigations. In comparison to gas engines the available sizes are not suitable, the required level of experience for the technology for this instance not given, the efficiency not as high and the overall costs not competitive.

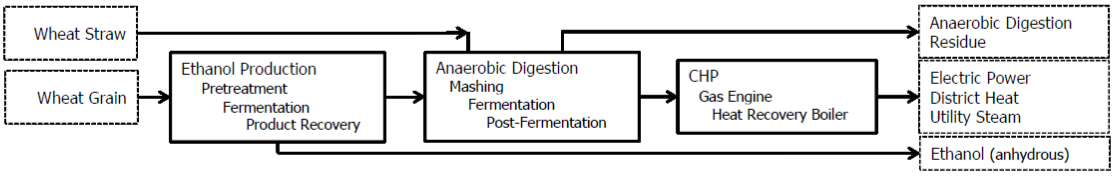
3.5. Polygeneration Process Definition

After the considerations presented in the earlier chapter five out of eight options remain. These five units are the building blocks for the polygeneration schemes assessed for the region under these premises. The quality attributes for the processes are the utilization of the full spectrum of available biomass, recycling of the not marketable product streams, a mixture of proven and promising future technology as well as synergistic effects of the units to increase the overall efficiency.

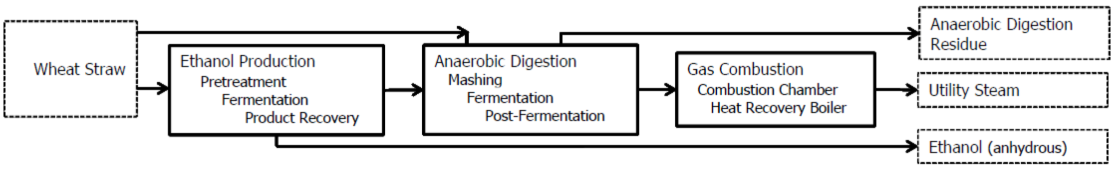
P1a: Ethanol from Wheat Grain, Biogas from Wheat Straw and Stillage utilized in a Combustion Chamber: This process is the leanest of the considered options. The ethanol process doesn't require extra utilities for the pretreatment and the stillage is converted to methane by means of anaerobic digestion along with the pretreated straw. The biogas' energy is then directly converted to steam in the combustion/boiler process.



P1b: Ethanol from Wheat Grain, Biogas from Wheat Straw and Stillage utilized in a Gas Engine : The process is completely self supplying except for the biomass input. Both heat and electricity are provided for by the specific unit operations. Due to the production of electricity the required amount of acreage will increase. The ratio of grain and straw input can be adapted by the engines electric output to reflect the realities on the field so that the available biomass is used to its full extent.



P2a: Ethanol from Wheat Straw (C6 only), Biogas from Wheat Straw and Stillage utilized in a Combustion Chamber: The equipment for pretreatment can be used for both ethanol and biogas fermentation. The biomass that is facilitated in the process is 100 % agricultural residue only. Therefore an added value is created complementing the usual agricultural products. Due to the lack of a generator the process is again dependent on external energy input. The biomass fed into the process is realized to a great extent. Sugars that are not suitable for ethanol fermentation (e.g. pentose) are consumed by anaerobic digestion.



P2b: Ethanol from Wheat Straw (C6 only), Biogas from Wheat Straw and Stillage utilized in a Gas Engine : The former process is supplemented with combined heat and power for electricity production. This is realized again in combination of ethanol and biogas fermentation based on wheat straw. By varying electric output and ethanol production target the wheat straw input can be influenced.

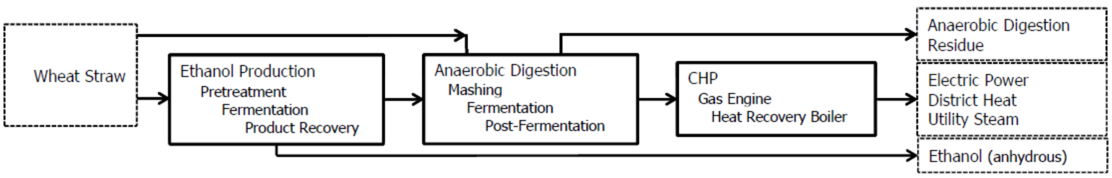


Table 5.1 gives an overview of the polygeneration process configurations later assessed.

4

ENGINEERING POLYGENERATION

This chapter highlights several specific issues of the polygeneration processes defined in Chapter 3. First, different options for lignocellulose pretreatment are introduced. The choice of raw material has a significant impact on the ethanol fermentation process. This process in conjunction with anaerobic digestion and the influence on the downstream process is surveyed. Last, the options for process integration are considered.

4.1. Pretreatment of Lignocellulose for Ethanol Production - Paper III

The main objective of lignocellulose pretreatment is to yield a product that can be efficiently utilized by the follow up enzymatic hydrolysis [38–40]. Factors influencing the enzyme performance are accessible surface area, lignin content and distribution, removal of hemicellulose and degree of crystallization of cellulose [41, 42]. A possible classification for lignocellulose pretreatment methods was proposed by Sun and Cheng [43]:

- Physical Pretreatment
  - **Mechanical comminution** [44]
- Physico-chemical pretreatment
  - **Steam Explosion** (autohydrolysis) or **Steam Pretreatment** with and without addition of acid catalyst (H2SO4) or SO2 [45–48]
  - **Ammonia Fiber Explosion** (AFEX) [49–51]
  - **Controlled pH** [52, 53]
  - **CO_2 Explosion** [54, 55]
- Chemical pretreatment
  - **Ozonolysis** [56, 57]
  - **Acid hydrolysis** [38, 58, 59]
  - **Alkaline hydrolysis** (Dilute NaOH pretreatment [43], Ammonia Recycle Percolation (ARP) [60], Lime [61])
  - **Oxidative delignification** [62, 63]
  - **Organosolv process** [64, 65]

- Biological pretreatment
  - **Brown-, white-, soft-rot fungi** [66, 67]

It has to be noted that some categories overlap such as Physico-chemical and Chemical pretreatment methods in conjunction with acid are overlapping. Furthermore the term pretreatment is generally used when followed by an enzymatic hydrolysis whereas hydrolysis such as in acid hydrolysis is used when no further enzymatic processing is required. In recent years efforts have been intensified to identify pretreatment methods for lignocellulose that are commercially viable by fulfilling the efficiency and cost criteria, also in respect to the subsequent processing steps. Methods that were proven to be promising are ARP, AFEX, Controlled pH as well as processes with diluted acid and lime [40].

As a contribution to this effort experiments with steam pretreatment equipment of improved design were conducted and summarized in Paper III. The primary goal was to consolidate two-step dilute acid hydrolysis (DAH) into a single step. This was tried to be achieved by a two-level temperature profile. By doing so the major drawback of two-step processes, the washing step in betweeen , would be circumvented [68]. Two-step steam processes (pretreatment and hydrolysis) are very efficient in regard to sugar yields and also result in low inhibitor levels. Enzymatic hydrolysis (EH) was conducted after the DAH to examine the remaining sugar potential for a later upgrade of the process. In

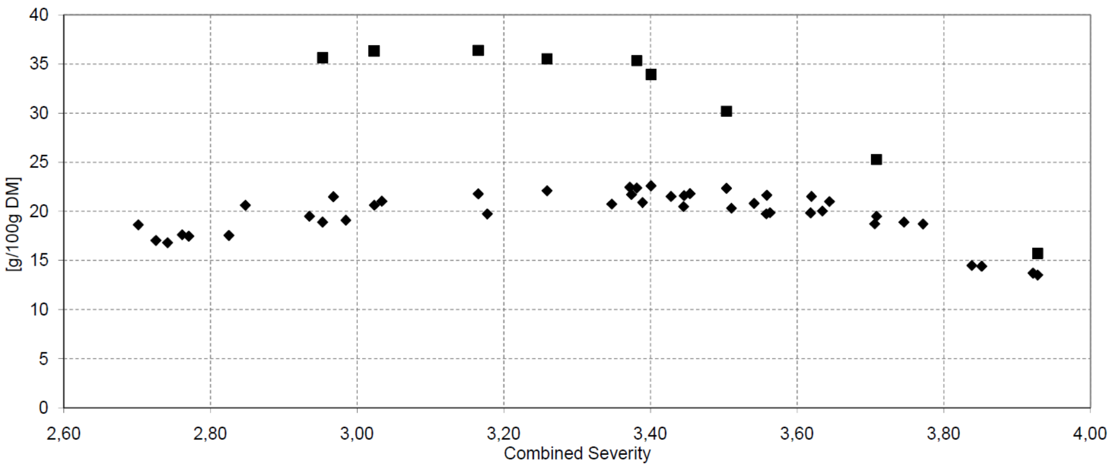


Figure 4.1: Sugars [g/100g]; ♦ total C6 sugars after DAH ■ total C6 sugars after enzymatic hydrolysis as function of combined severity; theor. max. 66.3 g C6/100 g DM

Figure 4.1 the C6 sugar yields after DAH and EH are shown as a function of combined

severity. Combined severity (CS) is a paramter used to describe the severity of a reaction in respect to temperature, time of the reaction and pH (details given in Paper III). The maximal hexose yield after DAH was 22.6 g C6/100g DM and after EH 36.4 C6/100g DM. The raw material contains 66.3 g monomeric C6/100g DM. Therefore about 55 % of hexoses are recovery after EH. The highest yields of pentoses were measured at lower severity due to degradation at higher intensities.
In comparison with experimental work based on Two-step pretreatment ([48]) 25 % less glucose was recovered after EH.

The knowledge gained from the experiments is of high value in the follow up process integration and simulation task. Although several promising pretreatment methods would be worth considering, the polygeneration processes are going to be based on diluted acid steam pretreatment followed by EH.

4.2. Ethanol Fermentation and Anaerobic Digestion of Stillage - Paper IV

Assuming wheat straw as raw material, the pretreatment process will yield a slurry containing unhydrolyzed substrate with regions of crystallized cellulose, fragments of lignin, hemicellulose and cellulose (polymers) as well as organic acids, monosaccharides, sugar degradation products and ash. After the pretreatment a neutralization of the slurry is necessary prior to enzymatic hydrolysis and fermentation.

Several design variants are available for sugar polymer hydrolysis and fermentation. The classic approach is separate hydrolysis and fermentation (SHF). As the name implies the enzyme step is isolated from the fermentation. A major advantage is that the conditions can be optimized for each task separately omitting the need to compromise on the question of temperature level (i.e. enzymatic hydrolysis 45-50°C, fermentation about 30°C) and pH that can influence the performance severely. Also the cell material can be recycled after fermentation. [45]
End product inhibition is a common problem with enzyme catalyzed processes lowering the final yield of fermentable sugars. This problem is intrinsic to the SHF process design. Simultaneous saccharification and fermentation (SSF) addresses this problem. The hydrolysis and fermentation take place simultaneously in the same vessel. The monosaccharides released by enzymatic hydrolysis are continuously consumed by the microorganism. Hence concentration levels that would reduce the performance of the

enzymes are prevented resulting in a high conversion rate and yield. The ethanol produced can reduce the activity of the enzyme [69]. At the concentration levels currently achieved this is not yet a major issue. Another two important issues are brought to attention by Galbe et al. [45]. First, the temperature level of 35°C poses a compromise between the optima of hydrolysis and fermentation but this drawback is expected to be overcome by the development of thermotolerant yeast strains. Second, there are implications on the engineering level. By reducing the process steps a reactor can be saved including all operational equipment. However, due to the fact that the slurry necessarily contains lignin yeast recycling is no longer an option.
Based on SHF and SSF consolidated bioprocessing (CBP) is a logical future development [70]. This process involves the production of saccharolytic enzymes (cellulases and hemicellulases), the hydrolysis of carbohydrate components present in pretreated biomass to sugars, the fermentation of hexose sugars (glucose, mannose and galactose) and the fermentation of pentose sugars (xylose and arabinose) and is envisioned to be facilitated by a single microorganism.

Raw material utilization is of paramount interest since it accounts for around 30 % of the specific production costs [71]. Saccharomyces cerevisiae is capable of fermenting hexose sugars such as glucose, mannose and galactose but has only very limited capabilities regarding pentose sugars. Due to the yeasts properties and long history for this application it is almost ubiquitously used in form of different strains for ethanol production. Properties required for industrial lignocellulosic ethanol production include ethanol productivity, ethanol tolerance, lignocellulose hydrolysate tolerance and tolerance to low pH. Industrial strains that are also capable of fermenting pentose sugars were surveyed with special emphasis to inhibitor tolerance, strain stability and ability to ferment hydrolysates [72]. The Industrial S. cerevisiae strain TMB 3400 is reported to achieve an ethanol yield of 0.18 g ethanol/ g xylose, 0.43 g ethanol/ g total sugar from spruce hydrolysate and 0.30 g ethanol / g total sugar from steam pretreated corn stover [73]. This compares well to the ethanol yield found with starch fermentation ranging from 0.45-0.48 g ethanol / g sugar in the raw material.

The fermentation broth consists of ethanol, cell mass, byproducts of the fermentation as well as the remainder of the hydrolyzate. This is mostly remaining sugar in monomeric and polymeric form as well as lignin, lipids, protein and ash. One possible strategy for stillage utilization from lignocellulosic raw material is incineration for steam utility generation and pelletizing of the excess. This is a reported viable option for softwood, salix and corn stover [74]. Especially the utilization of the lignin's energy potential makes this process very attractive. Wheat straw on the other hand is not suitable for this kind of treatment due to the reasoning given earlier.

Anaerobic fermentation to yield biogas with high methane content is another promising solution to salvage the residual energy potential in the stillage. Paper IV is concerned with the estimation of ethanol and methane yields of a combined process. Wheat straw was steam pretreated under various conditions and thereafter saccharified by enzymatic hydrolysis. Based on the glucose content the ethanol yield and the residual methane potential were calculated.
The results are shown in 7.2. With increasing ethanol yield the methane potential decreases. The maximal yield of ethanol was found at pretreatment conditions 200°C for 10 min with 0.2 kg/kg wheat straw DM or 80 % of theoretical maximum. After ethanol fermentation the residual methane potential was 121.4 l_N / kg wheat straw DM. The theoretically attainable methane yield of wheat straw is estimated to be 373.4 l_N / kg wheat straw DM.

A study related to this thesis by Bauer et al. ([75]) explores the methane potential of various substrates and mixtures thereof. An excerpt of the results with the most relevant data for this work is given in Table 4.1. The values were converted from l_N / kg volatile solids to l_N / kg DM to sustain consistency of units within the thesis.

Table 4.1: Methane potential of various Substrates and Substrate Mixtures

	Methane, theor. l_N / kg straw DM	Methane, exp l_N / kg straw DM	Yield l_N / l_N
Wheat stillage	486	399	82
Maize silage	421	328	78
Barley silage	415	347	84
Wheat straw, native	408	258	63
Wheat straw, pretr.[1]	428	345	81
Mixture 1[2]	433	337	78
Mixture 7[3]	472	353	75

[1] Steam pretreatment conditions 170°C,10 min
[2] Mixture 1: 20 % Wheat Stillage, 80 % Wheat Straw, pretreated
[3] Mixture 7: 17.9 % Wheat Stillage, 82.1 % Maize Silage

4.3. Product Recovery from Fermentation Broths

The fermentation broth or beer is the main product of ethanol fermentation process. Moreover CO_2 and heat are formed in the process. The recovery of the ethanol in the fermentation broth - often referred to as downstream process - is split in two processes. First, ethanol is distilled from the beer and then further concentrated close to the azeotropic point of the ethanol-water mixture. The dehydration is facilitated by a second, separated process unit that can efficiently overcome the difficulties associated with the azeotropic point.
The downstream process is a major consumer of energy in form of utility steam. This section discusses the implication of lignocellulose fermentation on the ethanol recovery as well as the options for dehydration. The following section will cover in detail the necessary adjustments in process design for a thermally integrated polygeneration plant.

4.3.1 Energy Requirement for Distillation

As already mentioned in Chapter 3 the ethanol concentration after fermentation based on starch reaches up to 16.5 wt% whereas broths from lignocellulose contain only 4-5 wt% ethanol. The implication in regard to energy consumption is shown in Figure 7.1. The energy demand is around 9 / 6 / 4 MJ per kg anhydrous ethanol at 3 / 5 / 10 wt% ethanol in the beer. At 3 wt% about one-third of the ethanol's energy content is required solely for the removal of water by distillation. Therefore the concentration of the sugar before fermentation as well as the fermentability of the substrate and the max. concentration the microorganism can sustain have a significant impact on the energy consumption of the overall process and hence energy yield. In this context 5 wt% ethanol in beer is often considered as the critical threshold.

4.3.2 Dehydration

Azeotropic Distillation

This process is among the longest established procedures to dehydrate ethanol. An additional solvent is introduced to the ethanol/water mixture. Due to differences in the solubility in the solvent is it possible to circumvent the azeotropic point and still remain with a distillation process. This allows for a convenient integration with the remaining product recovery process so that the energy consumption can be reduced. Even when applying measures to reduce the energy demand the operating costs will be three times higher than with dehydration by vapor permeation based on estimations by the author. For azeotrop rectification electricity, cooling and steam are contributing to the costs of operation with heat accounting for the largest share. In addition a supplementary substance is introduced into the process. This used to be benzene that was found to be carcinogenic and in succession substituted by toluene, pentane or cyclohexen.

Molecular Sieve

As a consequence of the problems associated with azeotrop distillation molecular sieve technology was established as state-of-the-art process for ethanol dehydration in large scale facilities. Water is adsorbed by zeolites while ethanol is excluded due to steric effects. Once the zeolites are saturated with water they are regenerated by applying low pressure and purified ethanol that functions as carrier for the desorbed water. This process is also known as pressure swing adsorption (PSA). The demand for steam utilities and therefore the operational costs are considerably lower than in the case of azeotrop distillation. A lifespan of more than 10 years also contributes to low costs. The ethanol quality attainable in respect to the dehydration performance is unparalleled. Drawbacks of molecular sieves are the discontinuous operation and the high initial investment costs. For ethanol dehydration the application is feasible for plants with a production target $\rangle$ 100.000 t anhydrous ethanol per year [76].

Membrane Technology

The high investment costs of molecular sieve technology renders it unattractive for small scale ethanol plants. Processes more suitable for this type of plantsare pervaporation and vapor permeation. These processes rely on a dense, hydrophilic membrane. Water is able to permeate through the membrane while ethanol is to the largest part retained in the retentate stream. In pervaporation the feed stream is liquid while it is vaporous in vapor permeation. In terms of costs of operations the membrane based processes are very economical although electric energy is required for cooling utilities and the vacuum pump. The membrane's life is about 3-4 years. The capacity of this process can be increased by linear addition of membrane modules. Since the module costs are a major cost factor only small economy of scale effects can be realized. Therefore the range of application is limited to small and middle scale ethanol plants. This could be improved by introducing membranes of high flux and selectivity, the two major parameters determining the membrane performance [77]. For membrane processes it is specific that the performance increases with higher water content in the feed. This can be exploited by varying the feed concentration obtained from the rectification in the range from 85-94 wt% .

To determine the performance of currently available membranes measurements were conducted with a membrane kindly provided by GKSS, Germany. The active separating layer was made of polyvinyl alcohol (PVA) with a polyacryl nitril (PAN) used as backing layer. Figure 7.2 and Figure 7.3 show measurement setups for pervaporation and vapor

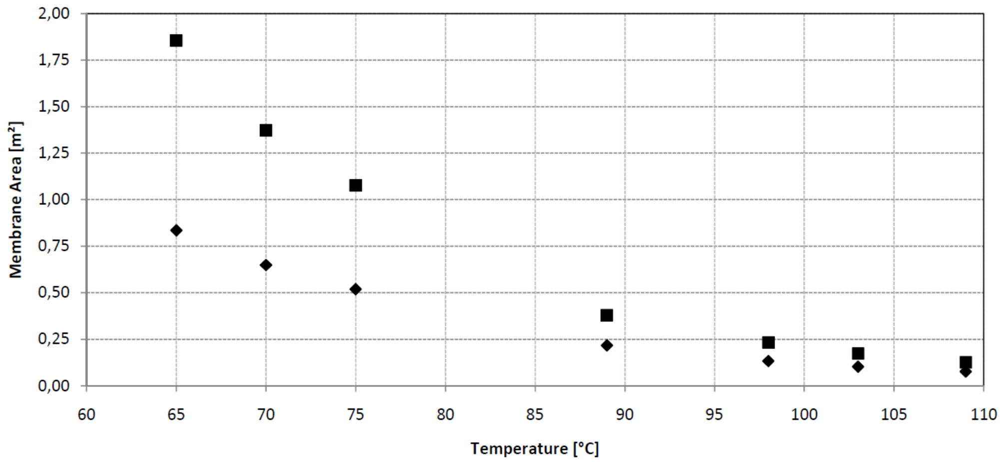


Figure 4.2: Membrane area requirement to dehydrate 1kg/h of 95 wt% ethanol to ♦ 99.0 wt% and ■ 99.7 wt% .

permeation used to determine the membrane performance under different conditions. One aspect examined in this work is the influence of feed temperature on the membrane performance. The total membrane area required to dehydrate 1kg/h ethanol/water mixture of 95 wt% ethanol was used as benchmark criterion. In Figure 4.2 the measurement points collected below 85 °C had a liquid feed stream (pervaporation), at temperatures above 85 °C the feed was vaporous (vapor permeation). The results of the examination demonstrate that the required membrane area rapidly declines with increasing temperature. For this type of membrane a maximum temperature of 120 °C is recommended. At higher temperature levels membranes based ceramics can be applied. Another aspect discussed is the final ethanol concentration. At lower water concentration the chemical potential is reduced due to the low partial pressure of water in the feed stream resulting in a loss of performance. To attain a final concentration of ethanol of 99.7 wt% compared to 99.0 wt% the membrane are has to be increased up to 122 wt% , that is more than twice the membrane area for 0.7 wt% less water. Also the power consumption is increased considerably.

4.4. Heat Integration by Pinch Analysis - Paper V

Heat consumption is a major concern for every ethanol process. The driving forces to reduce the energy uptake are economic aspects as well as the improved energy output to input ratio that is of special interest in a fuel production process. Increased heat consumption is often followed by higher cooling duties at a later point in the process.

Paper V analyzes the options for utility reduction of small scale ethanol production. Special emphasis is given to the downstream process since the size reduction from large scale plants has the largest impact on these unit. Also the prospects for energy savings are potentially high. The goal is achieved by means of pinch analysis. This is a widely used methodology for heat integration within processes that aims to reduce the demand for heating and cooling utilities [78, 79]. The process examined by the publication is similar to the proposed polygeneration process with gas engine except for the steam pretreatment unit. This is due to the fact that this examination took place at a very early stage when wheat straw was not yet considered as substrate for anaerobic digestion and ethanol fermentation.

4.4.1 Major Sources and Sinks of Heat Energy

Pinch analysis matches heat sources and sinks according to their temperature level. Therefore every analysis of this kind identifies them in the initial step.
The major sources of heat are:

- saccharification, yeast propagation and ethanol fermentation
- beer column, head product condenser
- rectification column, head product condenser
- gas engine, cooling circuit I & II motor
- gas engine, exhaust

The major sinks of heat are:

- mashing and liquefaction of starch
- preheating of beer for beer column
- beer column, reboiler
- rectification column, reboiler

4.4.2 Pinch Analysis

The pinch analysis was representatively conducted for the process with a ethanol production target of 1000 t anhydrous ethanol per year and 703 kW of electric power generated by a gas engine with distillation columns at ambient pressure. This is state of the art since beverage alcohol is mainly produced in ethanol processes of that size. The result is shown in Figure 4.3 at the top. The figure is characteristic for basic ethanol processes that require steam of high quality for the columns but yield low temperature streams in the upstream process. With this configuration the potential for heat transfer is very limited. The energy that can be transferred from hot streams to cold streams is only 192 kW. The cold target was found to be 749 kW, the hot target 451 kW.

A measure taken in large scale processes is to operate the rectification column not at

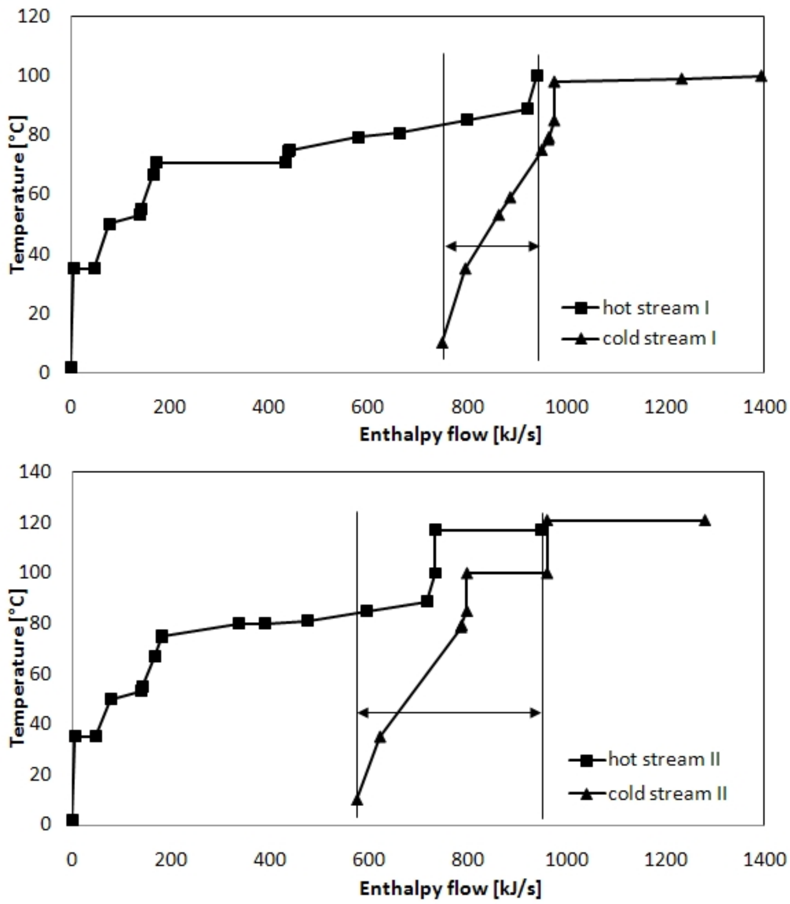


Figure 4.3: Pinch analysis of 1000 t/a ethanol process with rectification column at ambient pressure (top) and with pressurized rectification column at 4 bar absolute (bottom)

ambient pressure but well above. This has the advantage that the head product of the rectification column is at a temperature level that is adequate to power the reboiler of the beer column thereby saving most of the utilities for the condenser of the rectification head stream and the steam for the beer column reboiler.
Following this reasoning the pinch analysis was performed for the same process with a pressurized rectification column at 4 bar absolute. The bottom graph of Figure 4.3 confirms that this measure has a significant impact on the required utilities. The cold target is reduced 24 % to 575 kW, the hot target is 27 % less with 333 kW. The transferable heat increases by 92 % from 192 kW to 373 kW. The amount of heat provided by heat integration through heat transfer from hot streams to cold stream increases from 30 % to 52 % when pressurizing the rectification column.
Although this action is not commonly observed with ethanol processes of this size it is highly recommendable when considering fuel ethanol production.

The incorporation of steam pretreatment equipment will not change the analysis significantly. This is for two reasons. First, the unit is adequately isolated from the downstream process in this instance. Second, the temperature level of the utilities required for the steam pretreatment is a lot higher than for the remaining process. The output streams from this unit can be used to preheat the input therefore reducing its initial energy demand. By reducing the pressure in the reactor after pretreatment to 4 bar the heat in the flash vapor can be potentially used for distillation [71].

4.4.3 District Heat

Earlier the gas engine was identified as major heat source. The current process design usees part of the energy from the first cooling cycle to preheat the water for mashing (62.5 kW out of 400 kW). Due to the temperature level of 90°C the remaining heat can be fed into a district heating network. Nearby industries that have a year round demand such as producers of fruit juice would be ideal. With seasonal dependent consumers additional cooling capacity has to be installed.

5

PROCESS PERFORMANCE

The earlier chapters described the framework for energy carriers derived from polygeneration, established the viable possibilities and highlighted questions of engineering details. This chapter draws from the findings to determine the performance in respect to energy yield and economy of the considered scenarios. An overview of all polygeneration plant setups is given in Table 5.1.

Table 5.1: Overview Polygeneration Process Configurations

Process	Grain	Lignocellulose		Combustion	Gas
		C6	C5&C6	Chamber	Engine
P1a	X			X	
P1b	X				X
P2a		X		X	
(P2aC5)[1]			X	X	
P2b		X			X
(P2bC5)[1]			X		X

[1] Analysis limited to Chapter 5.2: Economy

5.1. Energy & Exergy - Paper VI

Of major interest in energy carrier production is the utilization of the provided energy in form of wheat grain and straw. Polygeneration processes have a multitude of energy input and output streams as the name already implies. These can contain chemical energy in form of wheat grain and straw, ethanol, methane, DDG and anaerobic digestion residue as well as physical energy such as electricity, district heat and utility streams of low quality.

A very common way to analyze the energy streams is by relying on heat of combustion for chemical energy that is then compared with physical energy such as electricity. The most common simluation programs provide this type of data as calculation output. This almost always leads to an overvaluation of biomass derived streams over electricity.

A different and better balanced approach is to examine the exergy content of different streams. The exergy is the amount of work a stream or system is maximal able to provide in reference to the surroundings. In other words not the total energy of a system but only the fraction that is actually available for work is considered. This is evidently very efficient when comparing streams of very heterogeneous nature such as found in polygeneration plants.
In Paper VI an analysis of the exergy flows for the processes defined in Chapter 3 is conducted. The calculations were based on an ethanol production target of 2500 t anhydrous ethanol per year as well as 1400 kW of electric power. The ratios of ethanol and electricity production of the smaller plant (1000 t anhydrous ethanol per year, 703 kW electric power) are almost equivalent can the major conclusions drawn from the analysis in the paper regarded as applicable for both sizes. In addition a traditional ethanol process with DDG production is introduced to benchmark the performance against a known process.

Exemplary Figure 5.1 shows the exergy flow of a polygeneration plant with ethanol and power production from wheat straw only (Process P2b). The conducted work confirms that the substitution of wheat grain with straw yields higher conversion efficiency losses from the net chemical energy stored in the lignocellulose to the product. This can be explained by the increased complexity of the substrate against rather homogeneous grain. It was also shown that due to this reason the full substrate spectrum must be incorporated. This would not be possible with an ethanol only process but is well provided for with the polygeneration schemes. Paper VI defines several efficiency factors to benchmark the systems different aspects. P1a and P1b can convince with a high degree of substrate utilization while P2a has the highest general efficiency due to the unutilized lignin fraction and some excess biogas. Processes with highly processed product streams like electric power or steam utilities have in general a higher amount of irreversibility. The unit responsible for the highest level of irreversibility is the thermal utilization of biogas in either a combustion chamber or a gas engine, not the fermentation processes. The highest specific ethanol output is found for process P1a. Close to 50 % of the total exergy input (grain + straw) of the process is recovered in ethanol. Electricity production requires an increased straw inputincreases, therefore P1b has an ethanol yield below 40 %. This figure drops further for P2a and P2b where only $\frac{1}{4}$ respectively $\frac{1}{5}$ are recovered in form of ethanol. This effect was anticipated due to the fermentation performance

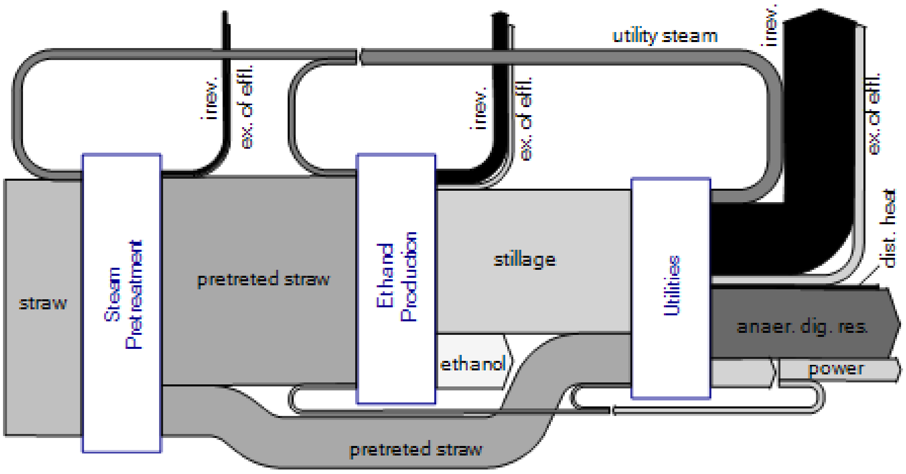


Figure 5.1: Exergy flow in a polygeneration plant. Ethanol from pretreated straw, utilities from stillage and pretreated straw via anaerobic fermentation, power generation, district heat, 2500 t anhydrous ethanol, 1400 kW electricity

without pentose sugar utilization. The factor Product I (definition see Paper IV) is more adequate to describe polygeneration processes since it doesn't isolate ethanol as product stream but also takes biogas and electricity into account. P1a retains the same value as for ethanol only but P1b (˜35 %), P2a (˜40 %) and P2b (˜ 30 %) improve considerably. None of the polygeneration processes is able to utilize the lignin fraction. Therefore a significant potential of energy remains untouched. After careful examination of all scenarios it becomes apparent that lignin utilization is a major future challenge.

5.2. Economy

This section covers the cost analysis of the polygeneration facilities. Therefore the four processes defined in Chapter 3 are estimated for two different sizes. The ethanol production targets of the processes are 1000 and 2500 t anhydrous ethanol per year. If the process incorporates a gas engine for ethanol production it is set for 700 kW respectively 1400 kW. The mass and energy balances of the processes were calculated by the simulation tool IPSEpro (see Chapter 3 and Paper I). The economic analysis was conducted with standard spreadsheet software as well as PSEconomy, an extension of the IPSEpro program package for investment costs determination. The analysis is extended by two additional processes to determine the impact of pentose fermentation to ethanol (P2aC5 and P2bC5).

5.2.1 Production Costs

Products of the polygeneration processes are ethanol, electricity, methane, district heat and anaerobic digestion residue. The rate for electricity fed into the grid is fixed. For reference see Chapter 2. The sales price of district heat is assumed to be 1 c€/kWh. The anaerobic digestion residue is transported back to the fields at the appropriate times in the year. The value of the residue is already considered in the sales price of the wheat straw and therefore doesn't generate revenue by itself. Process P2a and P2aC5 do not utilize all methane produced. The excess methane is valued at 3 c€/kWh reflecting current rates for gas in Austria. The discounted cash flow (DCF) approach is used to estimate the required revenue from ethanol sales. Assumptions for the DCF analysis are given in Table 7.4. Contributors to the final sales price of ethanol are the investment costs, operating costs and cost of capital as well as the revenue from other products such as electricity among others. The method further considers the corporate tax and the impact of inflation with a depreciation window of 10 years. In Figure 5.2 the specific production costs of the polygeneration plants for two sizes, 1000 and 2500 t/a anhydrous ethanol, are shown. The costs for wheat grain and wheat straw are subject to great fluctuations. Hence, the costs for raw material are singled out in the graph. In future this makes it easier to reuse the figures by readjusting it for the then valid sales prices of raw material. The remaining elements of the earlier described DCF method are summarized by the term "basic costs". The other elements are not subject to such high fluctuation. The cost for wheat grain and wheat straw is set to 130 €/t respectively 56.5 €/t reflecting market prices at the time of writing for grain as well as a base price for straw of 10 €/t plus labor, machines and transportation [80]. The configuration of the polygeneration process determines the amount of raw material used in the process. The share of wheat grain on the ethanol price for all starch-based ethanol processes in these scenarios is 0.37 c€/L. Measures, such as advanced hydrolysis, yeast propagation and fermentation control strategies, that would allow higher ethanol yields are not economically feasible for small scale ethanol production.

The same is true for wheat straw. P2a and P2aC5 (both without gas engine) have the same consumption of wheat straw (0.33 and 0.23 c€/L) when scaling up. The impact of increased column heat efficiency is only minor with a size increase of factor 2.5 and consequently not reflected in the final price. For processes with gas engine (P1b, P2b and P2bC5) the specific electricity output per unit ethanol is lower for the 2500 t/a (see process definition). Hence a reduction in wheat straw consumption of 5 c€/L is detected for the larger plants. Utilization of pentose in the ethanol fermentation has only

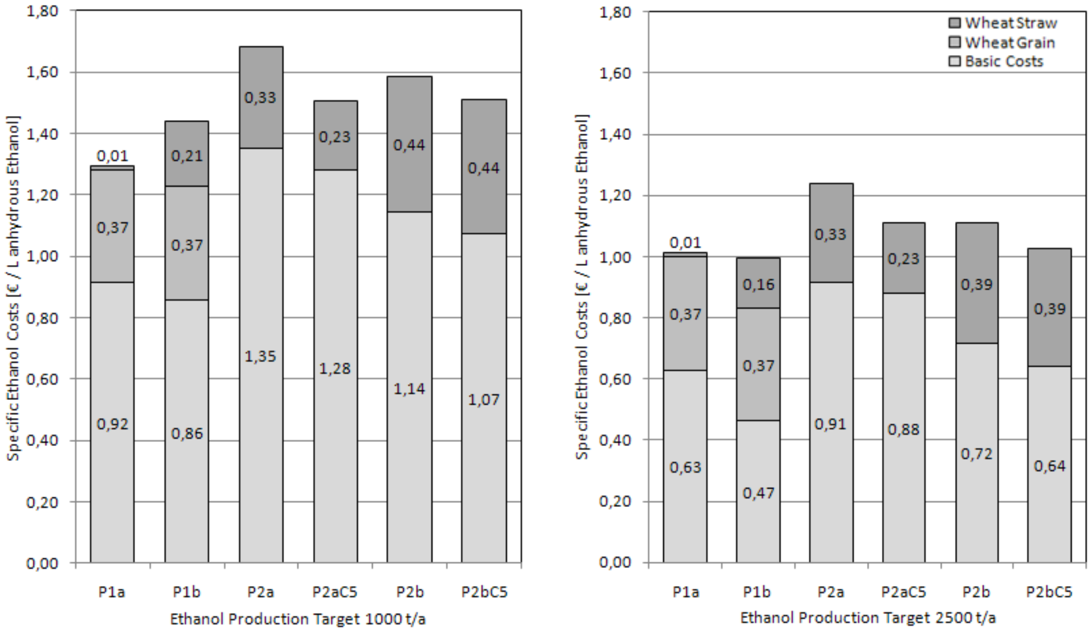


Figure 5.2: Specific production costs of ethanol for production targets of 1000 and 2500 t/a anhydrous ethanol

minor impact on the wheat straw demand as is demonstrated by P2b and P2bC5. Both processes generate the same specific costs for the ethanol price with 0.44 (1000 t/a) and 0.39 c€/L (2500 t/a). P2a (0.33 c€/L) and P2aC5 (0.23 c€/L) reflect differences in wheat straw uptake due to the process layout. The stillage from both ethanol processes is anaerobically digested to methane that is (a) utilized to produce the utility steam and (b) sold. Since P2a ferments only C6 sugars to ethanol more wheat straw is initially required to satisfy the demand. A side effect of pentose fermentation is the lower mass flow through the beer column reducing the heat duty.

The ethanol from the smaller plant is 28 to 49 c€/L more expensive then for the 2500 t/a plant. In the previous paragraph it was established that the increase of production by a factor 2.5 has only limited influence on the specific raw material consumption. Severely influenced are the operating costs, especially the specific amount of labor (detailed in the following section), and the investment costs. The reduction of ethanol production price after scale up is more pronounced for variants producing power. This can be attributed to the lower specific investment costs for the larger gas engine. Also the specific costs for the larger anaerobic digestion fermenter reduces the final price significantly. The analysis demonstrates that the design point of the polygeneration plants coincides with a band of sizes that is very sensitive in respect to the economy of the process. At 1000 t/a the lowest price for ethanol can be found with process P1a at 1.29 €/L. After scale up the specific ethanol price drops to around 1.00 €/L for P1a, P1b and P2C5.

5.2.2 Cost of Operation

Labor and raw material are the major contributors to the operating cost (see 5.3). Substrate for ethanol fermentation and anaerobic digestion account for 30 - 60 % of the costs while labor is around 35 % for 1000 t/a and 20 % for 2500 t/a. P2b has with 2.7 m€/a the highest, P1a with 2.2 m€/a the lowest cost of operation at 1000 t/a. Fermentation of lignocelluloses to yield ethanol is costly due to the high costs of enzymes. Cost of enzymatic hydrolysis and fermentation increases from around 4 % for starch- to 15-25 % for lignocelluloses-based processes. These costs are thought to decrease in the future since the specific activity of the enzymes has been steadily improved over the last years [81]. The costs for dehydration with membrane replacements among others is for all

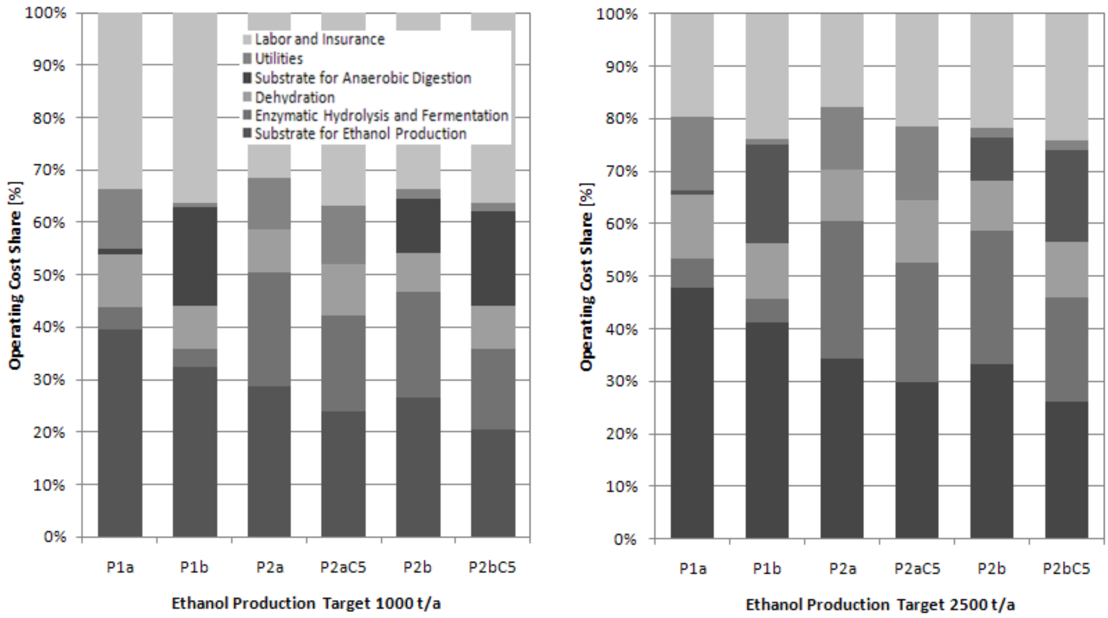


Figure 5.3: Share of plant operating costs for production targets of 1000 and 2500 t/a anhydrous ethanol

facilities around 10 %. Better process integration and materials that can accommodate high temperatures with better performance characteristics (flux, selectivity, replacement time) will reduce this figure in the future. On-site production of enzymes will not be feasibly because it will not pay off at this size. Facilities without power generation have utility costs that amount to 10-12 % of the costs.

5.2.3 Land Allocation

The high volatility of the internationalized food markets in recent years made land allocation for energy crop production a benchmark criterion. The amount of acreage used to grow the substrates for the processes at 1000 t/a is given in Figure 5.4. The largest amount of area to grow the feedstock is used for the schemes relying on wheat straw only in conjunction with energy production. Since wheat straw is an agricultural byproduct with a low energy density it is an ideal substrate for this type of process. It rather supplements than substitutes food production since the main product, the grain is still available. For facilities relying on starch as substrate the outcome is case dependent. P1a requires more acreage for grain than for straw due to the low amount of wheat straw required for energy production. Instead of stillage utilization by anaerobic digestion it

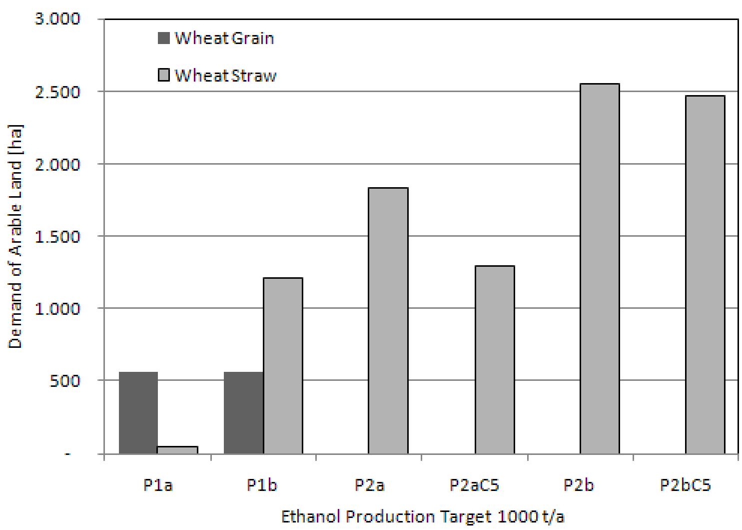


Figure 5.4: Acreage used for wheat grain and wheat straw production

could be dried to DDGS. The additional utilities could be provided by supplementary wheat straw. P1b requires more acreage for wheat straw production than for grain since electricity production demands additional wheat straw input. In regard to life cycle analysis the distance from the field to the facility is an important factor. This is especially true for wheat straw since its energy density is comparably low. P2b requires the most acreage of all scenarios. The ideal (100 % acreage utilized for production of raw material) transportation radius to the facility is 2.8 km (1000 t/a) and 4.3 km (2500 t/a) for P2b. This distance can still be handled logistically. The impact on the LCA for these scenarios remains to be proven.

5.3. Conclusion

Applying exergy analysis the starch-based ethanol process was found to have higher efficiencies. This was to a great part on account of the lignin fraction that remained unused. Pentose fermentation as in P2aC5 and P2bC5 is thought to have limited impact on the exergy analysis in terms of efficiencies. The raw material consumption is slightly lower for pentose fermenting ethanol plants since less material has to be processed in the downstream part resulting in lower utility demand. In conclusion thereof less methane and by that less straw for anaerobic digestion have to be supplied. However, this has but minor impact in relation to the total energy input. Apart from this issue more pretreated straw will bypass the fermentation process since less total wheat is required (both hexoses and pentoses are converted into ethanol). Since the exergy analysis did only deal with the input and output streams the defined efficiencies are only slightly different for P2aC5 and P2bC5.

The current rate for anhydrous ethanol is around 0.495 €/L (FOB ARA T2, [82]). None of the proposed polygeneration schemes is able to produce successfully at the going market prices. The most promising processes produce ethanol for double the rate at around 1.00 €/L. The difference in specific ethanol price of variants P1a, P1b and P2bC5 at 2500 t/a is marginal. The higher investment costs of P1bC5 are compensated for by the revenue from the electricity sales. By diversifying the process the level of risk involved with the enterprise is reduced. For pentose fermentation considerable room for improvement for industrial application remains. Until pentose fermentation is ready for the mass market ethanol would be 10% more expensive as was shown by P2b. P1a and P1b can be realized today since all process units are well investigated. Fermentation of hydrolyzed lignocelluloses is already applied in pilot and demo plants but requires further work to attain the level of experience that comes with starch fermentation. Especially the robustness of the microorganisms in regard to inhibitory substances yielded from pretreatment has to be observed. Pentose was found to be efficiently utilized by the anaerobic digestion unit in the considered polygeneration scenarios. Sassner et al. conducted a study on lignocellulosic ethanol production from spruce (softwood), Salix (hardwood) and corn stover. The stillage was dried and utilized for steam generation or pelletized and sold [74]. For plant about 50 times larger than the ones considered in this study the production costs were found to be competitive with going market rates. This is to a significant portion due to the revenue drawn from lignin utilization. A similar way to utilize lignin is used by the IBUS process where after distillation, the thin stillage is separated into two fractions, the solid biofuel, mainly consisting of lignin, and a fiber thin stillage containing water soluble substances [83]. Hereby is the solid biofuel fraction used in a CHP process while the fiber thin stillage could potentially be used for anaerobic degestion instead of animal fodder.

For the given scenario process P1b balances the requirements the best. The process is lean in terms of substrate since inputs are almost completely utilized as was shown with the exergy analysis. Acreage is still fully allocated to energy production but transport distances are kept at a minimum. The recycling of the anaerobic digestion residue returns substances of high nutritional value to the fields supporting the soil quality. The impact of anaerobic digestion residue recycling to the field was not accounted for. Since it substitutes part of the requirement for fertilizers it is worthwhile to examine the polygeneration plants by life cycle analysis. None of the proposed processes is able to facilitate the lignin fraction of wheat straw. Therefore a large potential is left idle. Utilizing lignin would improve the product yield of the process further given that the separation process can be designed efficiently especially in regard to energy demand. Vending lignin or products derived thereof can further improve the economic aspects contributing to break even against starch-based ethanol facilities. Once the lignin is efficiently used by the process in conjunction with a robust ethanol fermentation process that covers hexose and pentose it will prove superior in this analysis.

6

FINAL REMARKS & FUTURE WORK

This study has shown that issues with large scale ethanol production can be overcome by polygeneration in small scale. The transport distances are significantly reduced and the anaerobic digestion residue can be recycled to the field were mineral fertilizers are substituted. The energy self supply is also an important contributor underpinning the chosen methodology. On the other hand were some of the problem inherited from large scale facilities and found to be more pronounced with plants in a regional setting. Heat integration among others has to be executed in a less sophisticated way. Therefore the specific steam requirement of the ethanol recovery is increased. Further on site yeast propagation and enzyme production is not feasibly at this plant size.
However, size reduction creates possibilities for alternative options. Then membrane technology is superior in terms of price and performance at this size over molecular sieves. Since the plants are not as fine tuned as their big counterparts more flexibility in regard to processing is possible. This helps the operator to respond to changes in the market earlier. Polygeneration goes further. Multiple products mean multiple sources of income. In case one of the markets underperforms there are always others to back up the lost income. By increasing the size of the plant economy of scale effects would improve the economy of the process. An ethanol production target about double the current size appears realistic before transport distances and the size of anaerobic digestion fermenters start to be limiting.
One known problem of all surveyed polygeneration plants remains. There has not been found a strategy to incorporate and use lignin. Its high energy content and significant share in the raw material wheat straw makes it an imperative to use. In the current schemes it has no specific purpose but burdens the process with utilities. The development of strategies for lignin processing is without question one of the most pressing problems not just for the introduced facilities but for every process dealing with lignocelluloses in conjunction with ethanol fermentation.

Next to the energy and economical performance life cycle analysis would have been a valuable evaluation and decision tool completing the analysis of the processes. The exergy analysis was one step in this direction contributing core input parameters for the LCA. It would be necessary to fully understand the impact of polygeneration plants on the region. Life cycle analysis requires a high level of know-how and experience to create representative results. Since that was not disposable at the time the study was conducted it remains to be part of future work on this topic.

7

APPENDIX

Table 7.1: World Fuel Ethanol Production 2008 [84]

Country	[Mt]
USA	26.9
Brazil	19.3
EU	2.2
China	1.5
Canada	0.7
Other	1.2
Total	51.8

Table 7.2: Ethanol yield and Methane potential after preceding ethanol fermentation

Pretreatment cond.	Ethanol	Methane
	kg / kg straw DM	l_N / kg straw DM
Ethanol, theor. max.	0.249	187.8
Methane, theor. max.	0.000	373.8
160°C, 10 min	0.061	229.4
180°C, 10 min	0.087	207.9
180°C, 15 min	0.104	212.0
180°C, 20 min	0.131	161.4
200°C, 10 min	0.200	121.4

Table 7.3: Ethanol Standards of USA, Brazil and Europe

Properties	Unit	USA		Brazil		EU
		D 4806	**D 4806 Undenatured**	**Anhydrous**	**Hydrous**	**EN 15376**
Ethanol Content	wt %, min.	92	93.8	99.5[3]	–	[96.7]
Ethanol + C3-C5 sat. alc.	wt %, min	–	[98.3][2]	–	–	98.7
Total Alcohol	wt %, min.	–	[98.7]	99.5	93.9	[99.7]
C3-C5 sat. alcohols	wt, max	–[1]	[4.5]	–	–	2
Water content	wt %, max	1.3	1.3	[0.5]	[6.1]	0.3
Density at 20C	kg/m3, max	–	–	791.5	807.6	–
Methanol	wt %, max	0.5	0.53	–	–	1
Denaturant	wt %, min/max	1.96 / 5.0	No Denaturant	No Denaturant	No Denaturant	Set By Country
Hydrocarbons	wt %, max	–	–	3[4]	3[4]	–
Solvent-washed gum	mg/100 mL, max	5	5.3	–	–	–
Gum or Resid by Evap	mg/100ml, max	5 (washed gum)	5.3 (washed gum)	–	5 (unwashed)[5]	10 (unwashed)[5]
Electrical Conductivity	uS/m, max	–	–	500	500	–
Sulfate	mg/kg, max*	4	4.2	–	4	–
Inorganic Chloride	mg/kg, max	40	42.1	–	1	20
Copper	mg/kg, max	0.1	0.105	0.07	–	0.1
Sodium	mg/kg, max	–	–	–	2	–
Iron	mg/kg, max	–	–	–	5	–
Acidity	mg/L, max	0.007 (56)	0.0074 (58.9)	0.0038 (30)	0.0038 (30)	0.007
pHe		6.5 - 9.0	6.5 - 9.0	–	6.0 - 8.0	–
Phosphorus	mg/L, max	–	–	–	–	0.5
Sulfur	mg/kg, max.	30	5	–	–	10
Appearance		Clear & Bright	Clear & Bright	Clear & No Impurities	Clear & No Impurities	Clear & Bright

[1] Not specified by can be calculated for US. (Heavy alcohol content = 100 - ethanol content - methanol content - water content)
[2] Numbers in [ ] are calculated estimates and not specified limits
[3] Limit only applies to ethanol not produced by fermentation from sugarcane or ethanol contaminated by other types of alcohol
[4] Applies only to imported ethanol
[5] Procedures are likely different.

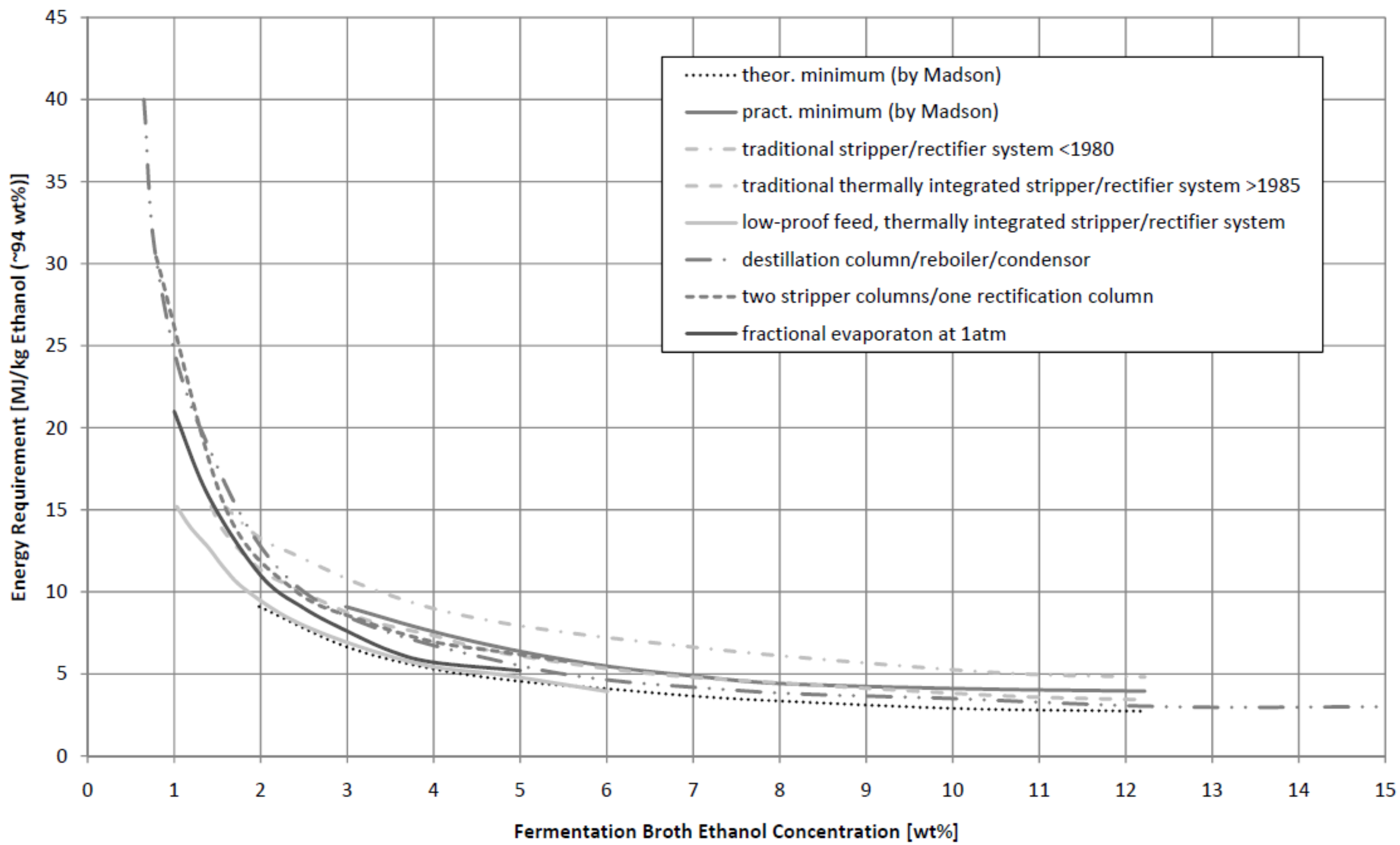


Figure 7.1: Energy Requirement for different distillation technologies as function of fermentation broth ethanol concentration, theor. minimum (by Madson) [10], pract. minimum (by Madson) [10], traditional stripper/rectifier system ⟨ 1980 [85], traditional thermally integrated stripper/rectifier system ⟩ 1985 [85], low-proof feed, thermally integrated stripper/rectifier system [85], destillation column/reboiler/condensor[86], two stripper columns/one rectification column[35], fractional evaporaton at 1 atm [87]

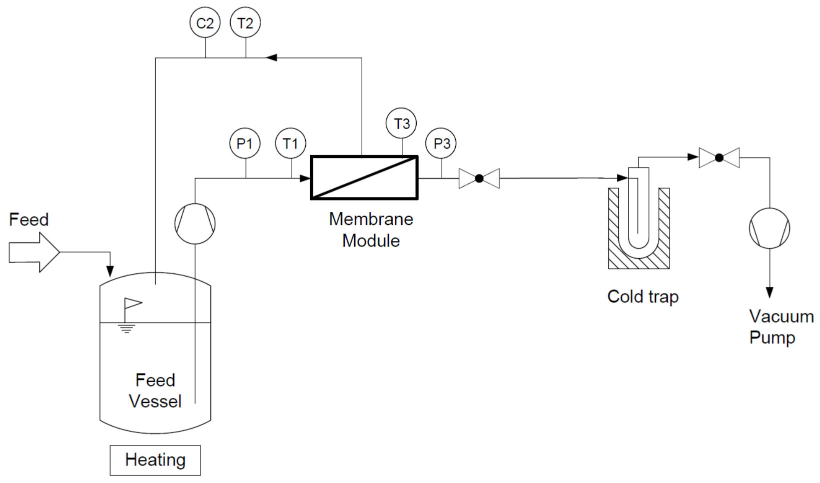


Figure 7.2: Pervaporation

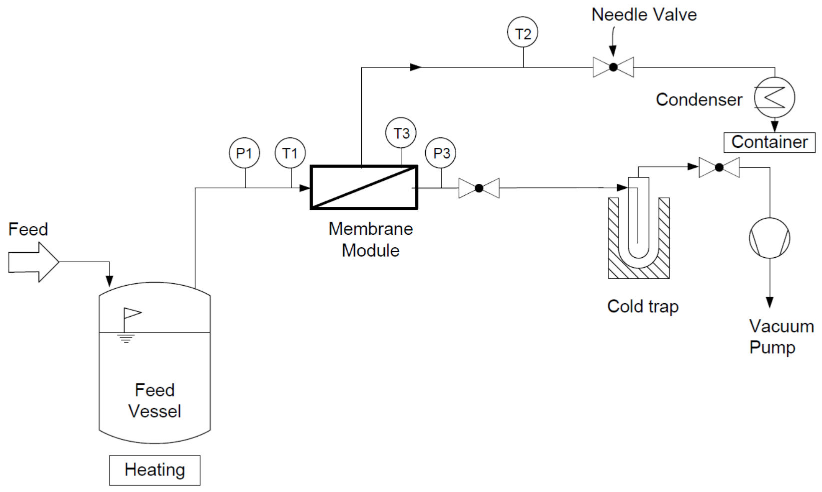


Figure 7.3: Vapor Permeation

Table 7.4: Parameters for discounted cash flow analysis.

Spilt Capital (Own / Borrowed)	20 : 80
Interest on Capital (Own / Borrowed)	7% : 6%
Discount Rate	4%
Inflation	3%
Corporate Tax	25%
Deprecation	linear, 10 years
Pay Back Peroid	10 years

8

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