Dissertation

# BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS – PROCESS SIMULATION, INTEGRATION AND VALIDATION

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

unter der Leitung von
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Wien, am 21.12.2012

Es ist nicht genug zu wissen – man muß auch anwenden.

Es ist nicht genug zu wollen – man muß auch tun.

*Johann Wolfgang von Goethe*

# KURZFASSUNG

Für ein nachhaltiges, österreichisches Energiesystem ist es unerläßlich den Verbrauch von fossilen Energieträgern zu reduzieren. Der Transportsektor spielt dabei eine wichtige Rolle, da er von Erdöl dominiert wird und damit ein maßgeblicher Verursacher von Treibhausgas-Emissionen ist. Nachhaltig erzeugte Biotreibstoff können einen wesentlichen Beitrag leisten um diesem Problem zu begegnen. Momentan werden die gesetzlich vorgeschriebenen Mengen an Biotreibstoffen durch Bioethanol aus Stärke und Biodiesel bereitgestellt. Für eine nachhaltige Lösung müssen jedoch auch andere Rohstoffe erschlossen werden. Die Technologie der Erzeugung von Bioethanol aus lignozellulosen Rohstoffen Holz und Stroh ist dabei vielversprechend, da diese einige Vorteile im Vergleich zu den konventionellen Rohstoffen aufweist.

Ziel dieser Arbeit ist es, die biotechnologische Produktion von Ethanol aus den Rohstoffen Holz und Stroh unter österreichischen Rahmenbedingungen zu untersuchen. Zur technischen, wirtschaftlichen und ökologischen Bewertung der Technologie wurden zunächst die 13 interessantesten Produktionskonzepte ausgewählt. Diese unterscheiden sich in erster Linie in der Art des Rohstoffs und der Art der Nebenprodukte. Mittels Prozesssimulation wurden im nächsten Schritt die genauen Massen- und Energiebilanzen für die einzelnen Konzepte berechnet. Die für die Simulation nötigen Modelle wurden teilweise im Rahmen dieser Arbeit erstellt. Durch Prozessintegration wurden Möglichkeiten zur Energieeinsparungen aufgezeigt. Deren Umsetzung führt zu energieeffizienten Prozessen, in denen die Prozesswärme durch einen Teil der Reststoffe bereitgestellt werden kann. Die erhaltenen Massen- und Energiebilanzen bilden dann die Grundlage für die Bewertung der Technologie. Dazu werden mittels Energieeffizienz-, Lebenszyklus- und Kostenvergleichsanalyse technische, ökologische und wirtschaftliche Aspekte der Technologie untersucht.

Die Ergebnisse der Arbeit zeigen, daß in allen untersuchten Konzepten Ethanol aus Holz oder Stroh energieautark produziert werden kann (ohne Zufuhr externer Brennstoffe) Zusätzlich könne aus den Reststoffen beträchtliche Mengen an Nebenprodukten gewonnen werden. Dementsprechend vielversprechend sind sowohl die Gesamtenergieeffizienzen der Prozesse (bis 78%) als auch die Reduktionen der Treibhausgasemissionen im Vergleich zu einem fossilen Referenzsystem (bis -76%). Die errechneten Ethanolkosten liegen mit 0.66 bis 0.94 € pro L Benzinäquivalent noch deutlich über den Kosten von Ethanol aus konventnionellen Rohstoffen. Dennoch erscheint es auf der Grundlage dieser Ergebnisse erstrebenswert, mittel- bis langfristig einen Teil des österreichischen Kraftstoffbedarfs durch Ethanol aus lignozelluloser Biomasse zu decken. Allerdings müssen hierzu noch einige technologische, logistische, wirtschaftliche und rechtliche Hindernisse zu überwunden werden.

# ABSTRACT

In a sustainable Austrian energy system, the consumption of fossil fuels has to be reduced. Particularly, the transport sector plays a vital role in this context, since it is dominated by the fossil energy carrier petroleum and thus contributes largely to the emission of Austrian greenhouse gases. The implementation of biofuels that are produced and used sustainably is one strategy to address this problem. At present, the mandatory amounts of renewable energy in the transport sector are provided by biodiesel and bioethanol from starch. However, for a sustainable long-term solution, other non-edible feedstocks need to be developed. A promising strategy to tackle that problem is the production of bioethanol from lignocellulosic raw materials, such as wood and straw. These raw materials have several advantages compared to the ones presently used.

The aim of this work is to investigate the biotechnological production of ethanol from wood and straw under Austrian boundary conditions. To assess technical, economic and environmental aspects of this technology, the 13 most interesting production concepts were selected. These concepts primarily differ in the type of raw material and the type of by-products that are obtained from non-fermentable process residues. Following the selection of production concepts, the mass and energy balances for the individual concepts were calculated by means of process simulation. The necessary unit models were partly developed within this work. Process integration methods were applied to identify options for heat recovery. Their implementation leads to energy-efficient processes in which process heat is provided by a part of the non-fermentable materials. The mass and energy balances thus obtained form the basis for the technology validation. For that end technical, environmental and economic aspects of the technology are examined using energy efficiency-, life-cycle- and cost comparison analysis.

The results of the study show that, energy self sufficient production of ethanol from lignocellulosic materials, i.e. without the provision of external fuels, is possible. In addition considerable quantities of by-products can be obtained from process residues. Accordingly, high overall energy efficiencies of the processes (up to 78%) and substantial reductions in greenhouse gas emissions compared to a fossil reference system (up to -76%) are obtained. With 0.66 to 0.94 € per L gasoline equivalent the ethanol costs lie still well above the cost of ethanol from conventional feedstocks. Based on these results, a long term strategy should aim at replacing a part of the Austrian fuel demand by ethanol from lignocellulosic biomass. However, before that more technological, logistical, legal and financing obstacles have to be overcome.

# ACKNOLEDGEMENT

I would like to thank my supervisor Prof. Anton Friedl for his support and for giving me the opportunity to work on an intersting topic and follow my own ideas. Morevover, I want to thank him for creating a uniquely positive working atmosphere.

I also want to thank Kurt Könighofer and Dr. Gerfried Jungmeier from JOANNEUM Research for the enjoyable collaboration.

A special thanks goes to my colleagues: to Ala for his support in pinch analysis and heat exchanger network synthesis, to Tino for his supporting calculations in APSENplus and for proof reading, to Antonia for proof reading and to Kian for his support in all administrative regards. I always have enjoyed sharing the office with you a lot.

I also want to thank Dr. Angela Miltner and Dr. Walter Wukovits for their patience and for their technical and administrative advice and everybody at the Research group and the Institute for the all the support and the warm atmosphere.

My parents Christine and Wolfgang deserve my deepest gratitude for their lifelong and everlasting support.

Most importantly, I thank Vera for her patience, understanding and support in the last eight years and many years to come and for enriching my life day by day.

# CONTENTS

# LIST OF PUBLICATIONS

The thesis includes the following peer reviewed publications:

| | |
|---|---|
| Paper I | Kravanja P. and Friedl A. (2010) Evaluation of ethanol from lignocellulosic biomass – Process scenarios for Austria. **Chemical Engineering Transaction** 21:1141-1146 |
| Paper II | Kravanja P., Modaressi A. and Friedl A. (2013) Heat integration of biochemical ethanol production from straw - A case study. **Applied Energy** 102:32-43 |
| Paper III | Kravanja P. and Friedl A. (2011) Process simulation of ethanol from straw – validation of scenarios for Austria. **Chemical Engineering Transaction** 25:863-868 |
| Paper IV | Lassmann T., Kravanja P. and Friedl A. (2011) Prozess-simulation der Produktion von Ethanol und Methan aus lignocellulosehaltigen Rohstoffen (in german)**. Chemie Ingenieur Technik** 83(10):1609-1617 |
| Paper V | Kravanja P., Könighofer K., Canella L., Jungmeier G. and Friedl A. (2012) Perspectives for the production of Bio-ethanol from Wood and Straw in Austria -Technical, economic and ecological aspects. **Clean technologies and environmental policies** 14(3):411-425 |

Author's contribution to the papers:

| | |
|---|---|
| Paper I | I did all the work. Anton Friedl read and approved the paper. |
| Paper II | I wrote and designed the study. I performed process design and simulation, data extraction and analyzed results.<br>**The contribution of other authors:** Ala Modarresi carried out pinch analysis and heat exchanger network synthesis. Anton Friedl read and approved the paper. |
| Paper III | I did all the work. Anton Friedl read and approved the paper. |
| Paper IV | I assisted in designing and writing the paper, performed process simulation and energy analysis.<br>**The contribution of the first author:** Tino Lassmann designed and wrote the paper. Anton Friedl read and approved the paper. |
| Paper V | I wrote and designed the study and analyzed the results. I developed concepts, performed process design and simulation and energy analysis.<br>**The contribution of other authors:** Kurt Könighofer performed economic evaluation. Lorenza Canella performed LCA. Gerfried Jungmeier and Anton Friedl read and approved the paper. |

# ABBREVIATIONS

| | |
|---|---|
| AD | Anaerobic digestion |
| AP | Atmospheric pressure |
| CBP | Consolidated bioprocessing |
| CHP | Combined heat and power |
| COD | Chemical oxygen demand |
| CSTR | Continuosly stirred tank reactor |
| DM | Dry matter |
| FPU | Filter paper units |
| HENS | Heat exchanger network synthesis |
| HRT | Hydraulic retention time |
| IU | International unit |
| GHG | Greenhouse gases |
| GMO | Genetically modified organism |
| LCA | Life cycle analysis |
| LHV | Lower heating value |
| MP | Medium pressure |
| OLR | Organic Loading Rate |
| SHF | Separate Hydrolysis and Fermentation |
| SSCF | Simultaneous Sacchirifcation and Co-Fermentation |
| SSF | Simultaneous Sacchirifcation and Fermentation |
| UASB | Upflow anaerobic sludge blanket |
| WIS | Water insoluble solids |

# I. BACKGROUND

# 1 INTRODUCTION

## 1.1 MOTIVATION AND BACKGROUND

The Brundtland commission defined **sustainable development** as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs [un1, 1987]." Sustainable development rests on the three pillars economic growth, environmental protection and social equality, and even though it has been on the political agenda for a quarter century, mankind is still far away from reaching the desired state, where sustainable development can be guaranteed.

Energy services play a key role in modern society. They are indispensable for increasing the standard of living of less developed countries and maintaining the lifestyle in well developed countries. Unfortunately the present energy system is not sustainable. Non-renewable energy carriers, which dominate today's supply, are by definition not sustainable. Certainly, large profits are generated by the extraction of fossil resources. However, social equality and environmental protection cannot be attained relying solely on fossil energy. Only very large companies have the know-how for their extraction and conversion and the huge profits made are distributed among the share-holders, typically already very wealthy people. Accessing fossil resources becomes increasingly difficult, which results in a higher risk for accidents and more severe environmental impacts of extraction. The exploitation of tar sands and shale gas and the massive oil spill in the Gulf of Mexico in 2010 impressively exemplify this trend. During the conversion of fossil resources ever increasing amounts of greenhouse gases are emitted, affecting our climate irreversibly [Bernstein *et al.* , 2007]. Shifting to renewable energy is thus a key strategy in sustainable development [Dincer, 2000].

More than any other sector, transport is dominated by fossil energy carriers and consequently poses a particular challenge to sustainable development in general and climate protection and energy security in particular. In 2009, petroleum provided 94% of worldwide energy in the transport sector [iea, 2011a] resulting in substantial emissions of greenhouse gases. Moreover, petroleum reserves are concentrated in very particular regions of the globe which negatively affects the security of supply and is partly responsible for the high volatility of the oil price. In 2010, 54.4% of proven oil reserves were located in the Middle East [bp2, 2011].

**Biofuels** are produced from local and renewable resources and can therefore in principle be a remedy to the negative effects of fossil fuels. However, there has been a lively discussion, whether introducing biofuels to our energy system actually shows the desired effects. Concerns were raised about the negative effect on food prices and about the actual capability of biofuels to reduce $CO_2$-emissions, just to name the most prominent ones. As a positive result of this discussion, sustainability aspects became a big issue on the agenda of the bio-fuel community, as expressed in various efforts to assure and certify the sustainability of bio-energy systems [van Dam *et al.* , 2010]. In Fig. 1-1, sustainability issues of biofuels are summarized.

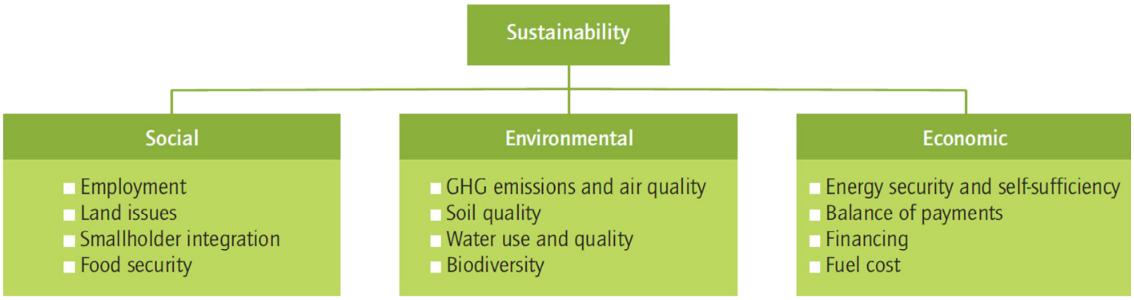

*Fig. 1-1: Sustainability aspects of bio-fuel and bio-energy production. Source: [iea, 2011b]*

For the biofuels of the future a good performance in all aspects social, environmental and economic, is thus mandatory. Oftentimes only greenhouse gas emissions, production cost and food security are considered, however, the other sustainability criteria should not be neglected. Today it is believed, that these criteria can be met and that biofuels, particularly the ones that are based on lignocellulosic feedstock, can actually contribute to a sustainable development [iea, 2011b].

In this respect, bio-ethanol produced from the **lignocellulosic residues wood** and **straw** is a particularly promising candidate. Cellulose, is the most abundant component in plant biomass [Lynd *et al.* , 2002] and also the most abundant organic molecule in the world [Esterbauer *et al.* , 1991]. Food security and land use should not be affected negatively as long as residual biomass is used. Moreover, the environmental burden can be kept low, when process residues are used to provide process heat; energy security can be attained via usage of local biomass. As a consequence, bio-ethanol from wood and straw is deemed to play a vital role in the future [iea, 2011b].

## 1.2 BIOFUELS AND BIOREFINERIES

Biofuels are defined as liquid and gaseous fuel for transport produced from biomass – organic matter derived from plants or animals [eu2, 2003b]. As can be seen in Table 1, a wide range of fuels produced from various feedstock falls into this category.

*Table 1: Biofuels, feedstock and conversion technologies. The technology covered within this work is highlighted in bold characters. Adapted from [fnr, 2009, eu2, 2003b, iea, 2011b]*

| **Biofuel** | **Feedstock** | **Process** |
|---|---|---|
| Biodiesel, Fatty acid methyl ester (FAME) | Rapseed oil, soy oil, palm oil, used fats, jatropha oil<br>Algae | Trans-esterification of oils to FAME |
| Pure vegetable oil | Rapseed, soy, used fats<br>Algae | Pressing and conditioning |
| Biomass to liquid (BtL) fuels, synthetic biofuels | Lignocellulose | Gasification and synthesis |
| Hydrogenated oils and fats | Various oils and fats | Co-processing, hydro-processing |
| Sugar-based hydrocarbons | Various sugar sources | Fermentation |
| **Bioethanol** | Grains, sugar beets, sugar cane, cassava<br>**Lignocellulose** | **Hydrolysis, fermentation and distillation** |
|  | Lignocellulose | Gasification and fermentation |
| Mixed alcohols | Lignocellulose | Gasification and synthesis |
| Biobutanol | Sugar, strach, Lignocellulose | Bacterial conversion |
| Biomethanol | Lignocellulose | Gasification and synthesis |
| Bio- Ethyl tert-butyl ether (ETBE) | Ethanol, fossil isobutene | Ethanol production + chemical synthesis |
| Bio- Methyl tert-butyl ether (MTBE) | Methanol, fossil isobutene | Methanol production + chemical synthesis |
| Biodimethylether (DME) | Lignocellulose | Gasification and synthesis |
| Biogas (Biomethane) | Energy crops, grasses, manure, organic wastes, waste water | Anaerobic digestion and upgrading |
| Biohydrogen | Any type of biomass | Fermentation, Gasification and synthesis, Biogas reforming |

Today, the most prominent biofuels already produced at a commercial scale are i) bioethanol produced from starch and sugar crops, ii) biodiesel produced from oils and fats and iii) biogas produced from energy crops, organic residues and waste waters. The worldwide promotion of biofuels (see section 1.3) gave rise to intense research and development efforts in the field. As a consequence various new feedstock, technologies and products came into play, whose sheer amount results in a need for classification.

A common feedstock-based classification distinguishes between first and second generation biofuels, where the term **first generation** summarizes today's commercially available biofuels that are primarily produced from crops such as grains, sugars or oils. **Second generation** biofuels are produced from non-food feedstock [iea, 2008] and can be further categorized upon the conversion technology, distinguishing between biochemical, thermochemical and hybrid technologies [iea, 2012a]. However, the terms first and second generation are slightly misleading, because they imply that the first generation technologies will eventually be entirely replaced by a superior second generation. Since this is not the case a more recent classification from IEA Bioenergy[1] was introduced. This classification is based on technology maturity [iea, 2011b] and uses the terms conventional and advanced. In this classification the term **conventional** is used for those biofuels that are presently produced at a commercial scale, whereas **advanced** biofuels are still in research and development. It must be noted, that advanced biofuels do not necessarily outperform conventional biofuels with respect to the sustainability criteria listed in Fig. 1-1. Consequently, in the future the best conventional and advanced technologies are envisioned to co-exist [iea, 2011b]. Moreover, one should bear in mind that this classification is a dynamic one. A technology that is today advanced may be conventional in a few years time.

There are several conventional and advanced processes available or in development, in which non-energy co-products are obtained with the bio-fuel. The value added by complete utilization of the biomass typically affects production economics positively. For these production systems the term **bio-refinery** is used. Including the by-products complicates the classification for bio-refineries further. Hence, a systematic classification is required. IEA Bioenergy adopted a biorefinery classification approach, which is based on the four features i) Platforms, ii) Products, iii) Feedstock and iv) Processes [Cherubini *et al.* , 2009]. Platforms are the intermediates between raw material and end product and play the most important role in the classification.

According to the above defined classifications either of the following terms can be used to describe the processes considered in this work:

i. Second generation ethanol using the biochemical route
ii. Advanced ethanol produced via the biochemical route.
iii. Three-platform (C6 sugars, C5 sugars, lignin) bio-refinery for ethanol and by-products

## 1.3 BIOFUEL LEGISLATION AND ETHANOL PRODUCTION

The high expectations regarding the positive effects of biofuels on energy security and greenhouse gas mitigation resulted in world-wide policies promoting bio-fuel production and use. In practice, blending mandates and targets as well as tax exemptions are the preferred support mechanisms.

Accordingly, the European Parliament adopted the EU directive 2003/30/EC, the so called **Biofuels directive** [eu2, 2003b] in 2003. This directive prescribes member states to

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[1] *IEA Bioenergy is an organisation set up in 1978 by the International Energy Agency (IEA) with the aim of improving cooperation and information exchange between countries that have national programmes in bioenergy research, development and deployment [iea, 2012b].*

ensure that 5.75%, based on the energy content, of total transport fuels on the market have to be biofuels by 31 December2010. In addition, the EU council directive 2003/96/EC, the so called **Energy taxation directive** was established enabling member states to grant tax reduction or exemptions for biofuels [eu2, 2003a].

In Austria, the **Energy taxation directive** and the **Biofuels directive** were transposed into national law [oen, 1994, bmf, 2005], [bml, 2004]. As a result, today biofuels are exempted from the fuel excise tax and the 5.75% blending target was reached duly [Winter *et al.* , 2011]. The consumption of transport fuels in Austria for the year 2010 is shown in Fig. 1-2.

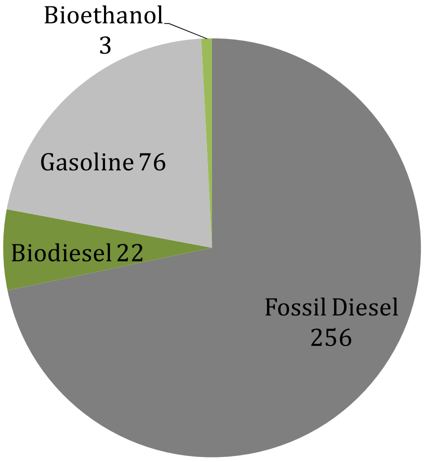

*Fig. 1-2: Energy provided by petroleum fuels to the Austria transport sector in 2010. Values are shown in PJ. Adapted from [Winter* et al. *, 2011]*

It immediately becomes clear, that the Austrian transport sector is dominated by diesel fuels (fossil and biodiesel) that provide some 78% of energy of Austrian transport fuels. The prescribed biofuel target was slightly exceeded; the energy based biofuel share amounted to 6.58% instead of the prescribed 5.75% and was achieved using approx. 500'000 t of biodiesel and 100'000 t of bioethanol [Winter *et al.* , 2011]. However, due to technical restrictions[2] bioethanol provides less than 4% of energy consumed in Austrian petrol vehicles.

Austrian bioethanol production presently takes place in one starch based facility in Pischeldsdorf, Lower Austria, whose annual ethanol production capacity amounts to 191'000 t. The actual production in 2010 totaled to 159'000 t [Winter *et al.* , 2011]. In Austria, the current blending target can thus easily be fulfilled using domestically

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[2] *The European Norm EN 228 allows a maximum share of 5 v/v% ethanol in unleaded gasoline.*

produced bioethanol. However, in the EU this situation is quite unique. Even though Austria is a very small country, in 2009 it was the world's 12th largest ethanol producer and Europe's 4th largest producer, as shown in Table 2. Austria's production capacity exceeded the combined production of UK and Italy, whose populations sum up to the fifteen fold of Austria's population As a consequence Austria is one of the few net exporters of ethanol, whereas the EU 27 as a whole remain net ethanol importers, mainly from South and Central American countries [epu, 2012].

*Table 2: Worldwide ethanol production in 2009 by country. Source: [ene, 2012]*

| **Country** | **Production** | |
|---|---|---|
| United States | 31'301 kt | 54.3% |
| Brazil | 19'422 kt | 33.7% |
| China | 1'599 kt | 2.8% |
| Canada | 1'051 kt | 1.8% |
| France | 975 kt | 1.7% |
| Germany | 585 kt | 1.0% |
| Spain | 363 kt | 0.6% |
| Thailand | 313 kt | 0.5% |
| India | 273 kt | 0.5% |
| Colombia | 242 kt | 0.4% |
| Australia | 172 kt | 0.3% |
| Austria | 140 kt | 0.2% |
| Sweden | 137 kt | 0.2% |
| Poland | 129 kt | 0.2% |
| Hungary | 117 kt | 0.2% |
| Others | 866 kt | 1.5% |
| **TOTAL** | **57'685 kt** | **100.0%** |
| **of which EU** | **2'446 kt** | **4.2%** |

Moreover, the 5.75% target was only a first milestone towards continuously increasing shares of renewable energy in European transport. In 2009 the **Renewable energy directive** 2009/28/EC [eu2, 2009a] was adopted prescribing 10% of renewable energy in the European transport sector by 31 December 2020. In order to boost advanced biofuel technologies the contribution from biofuels produced from wastes, residues, non-food cellulosic material, and ligno-cellulosic material counts twice towards the 10% mandate. In contrast to the 5.75% target from 2003, the 10% share until 2020 is mandated and thus legally binding. Moreover the Renewable energy directive defines sustainability criteria that have to be fulfilled by biofuels consumed in the EU [ec2, 2012, epu, 2012]. Another important document regarding biofuel legislation in the EU is the **Fuel quality directive** 2009/30/EC [eu2, 2009b], defining quality criteria for fossil fuels consumed in the EU.

Among others, it obliges fuel suppliers to reduce greenhouse gas emissions from fossil fuels by 6% [3] until 31 December 2020. Of course, a key strategy to achieve this reduction is blending of biofuels.

At the time of writing this thesis, the legislative procedure implementing the Renewable energy directive and the Fuel quality directive in Austria, is still in progress. From what was said before, it becomes clear, that biofuels and in particular advanced biofuels produced from lignocellulosic biomass are destined to play a vital role in a sustainable energy system of the future, which (this statement) is also supported by worldwide policies promoting the use of biofuels [iea, 2011b].

## 1.4 GOAL AND OUTLINE OF THIS WORK

As outlined in previous sections, EU energy policies aim at increasing the share of biofuels in the transport sector. Conventional ethanol will not suffice to reach the mandates and targets that were set, hence other feedstock and technologies will have to be tapped [iea, 2011b].

This thesis deals with the production of lignocellulosic ethanol in Austria. Its contents were developed within a joint research project between JOANNEUM Research GmbH and the Vienna University of Technology (FFG Project Number 818921) whose aim was to assess the Austrian perspectives for ethanol production from wood and straw [Könighofer *et al.* , 2012]. To that end, the following steps were applied:

i. **Technology review:** A state of the art technology review forms the basis for a further, detailed analysis of the technology. Based on the technology review the most promising and relevant production concepts are selected and modeling parameters for process simulation are determined.
ii. **Development of production concepts:** At present, the technology is not mature yet and many technological options exist. For an assessment of the technology the most relevant production concepts in an Austrian framework have to be singled out.
iii. **Process simulation and process heat integration:** For an assessment of the technology detailed mass and energy balances of the process are necessary. These balances are obtained by means of process simulation. To ensure energy efficient processes process heat integration methodologies are applied.
iv. **Technology validation:** The detailed mass and energy balances are used for technology validation. Process energy efficiency, life cycle greenhouse

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[3] *The reference value is the fuel baseline standard as defined in the Fuel quality directive.*

gas emissions and ethanol production costs are the parameters used to that end.

As in the FFG research project, the above listed workflow was applied in this thesis. However, certain aspects of the research project are in the focus of this thesis. Namely, these are the technology review, the development of production concepts and process simulation and heat integration. These are the parts of the project that were handled by the author of this thesis. For completeness, a brief summary of the technology validation, which was mainly performed by the research partners at JOANNEUM Research, is also included in this thesis.

The thesis is divided into four sections: Section I includes a general introduction, the technological background and the methodology applied. In section II the resulting papers are presented. In section III the most relevant findings are summarized and conclusions are drawn and section IV, the Appendix section, covers the model development and modeling details.

# 2 BIOTECHNOLOGICAL ETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

This section provides the data basis necessary for technology selection and process simulation. It contains i) information about Austrian biomass resources and ii) a review of the technologies available for lignocellulosic ethanol production.

First, in section 2.1 biomass resources for lignocellulosic ethanol production in Austria are discussed. Next, in section 2.2, an overview of the technology is given. Technical particularities and challenges in comparison with conventional ethanol production from grains and sugar cane are dealt with. Then, in section 2.3, the main part of section 2, the unit operations for biotechnological ethanol production from lignocellulosic biomass are reviewed. Finally, in section 2.4 potential by-products of the process are summarized.

## 2.1 AUSTRIAN BIOMASS RESOURCES FOR LIGNOCELLULOSIC ETHANOL PRODUCTION

To estimate the amount of lignocellulosic ethanol that could be produced in Austria, two parameters are needed: i) the potential of a certain type of biomass and ii) its theoretical ethanol yield, which can be derived from its composition. These parameters are shortly examined in the following.

### *2.1.1 BIOMASS POTENTIAL*

When talking about the potential of a resource, one can distinguish between the technical and the economic potential, where the **technical potential** describes the amount of a resource that is available considering technical, structural and ecologic restrictions. The **economic potential** is defined as the share of the technical potential that can be delivered at economically profitable levels [Kaltschmitt *et al.* , 2009]. The economic potential is a highly volatile number and hard to quantify. To do so detailed demand modeling is required. As a consequence the economic potential is not covered in this work. Instead estimates for the technical potential are briefly discussed for woody and herbaceous biomass.

For **woody biomass** the potential can be derived from the unused wood increment and the respective share of the most prominent softwood and hardwood species in Austria, spruce and beechwood. The unused wood increment is calculated as the difference between the total wood increment (i.e. that amount of wood that is growing in Austria in a one year period) and the annual amount harvested. The resulting potentials for the year 2006 are calculated assuming 50% availability and are listed in Table 3. A conversion from volumetric to mass based potential is necessary. As can be seen the potentials amount to some 380 kt/y for spruce and 90 kt/y for beechwood. Even though only 50% of availability is assumed, these figures have to be considered with caution. The amount of wood that is annually harvested in Austria is a highly volatile number [bml, 2012]. As a result the potential for bioethanol production is fluctuating strongly too. In addition to that, an increase in the demand for woody biomass is expected in Austria [Kranzl & Haas, 2008]. Therefore, one can conclude that the woody biomass potential in Austria is a rather uncertain number. In particular, the limited potential for beech suggests that **spruce** is the only type of woody biomass that shall be considered for ethanol production in Austria.

*Table 3: Potential of woody biomass for the base year 2006*

| Item | Value | Reference |
|---|---|---|
| Unused wood increment | 2.8 Mio. $m^3/a$ | 1, 2 |
| Share of spruce | 54% | 1 |
| Share of beech | 10% | 1 |
| Conversion factor spruce | 0.5 dry $t/m^3$ | 3 |
| Conversion factor beech | 0.7 dry $t/m^3$ | 3 |
| Availability | 50% | |
| Potential spruce | 377 dry kt/y | |
| Potential beech | 91 dry kt/y | |

*References: 1: [bml, 2012], 2: [bfw, 2012], 3: [Kaltschmitt* et al.*, 2009]*

The most abundant types of **herbaceous biomass** in Austria are wheat straw and maize straw. To calculate their technical potential, the annual grain yields and grain/straw ratios are considered. In Table 4 the data basis and the resulting potentials are listed.

*Table 4: Potential for straw biomass for the base year 2008*

| Item | Value | Reference |
|---|---|---|
| Annual wheat production | 1690 kt/y | 1 |
| Annual maize production | 2147 kt/y | 1 |
| Grain/straw ratio maize | 1:0.9 kg/kg | 2 |
| Grain/straw ratio wheat | 1:1.5 kg/kg | 2 |
| Annual wheat straw production | 1521 kt/y | |
| Annual maize straw production | 3221 kt/y | |
| Availability | 20% | |
| Dry matter content straw | 90% | |
| Potential wheat straw | 274 dry kt/y | |
| Potential maize straw | 580 dry kt/y | |

*References: 1: [sta, 2011], 2: [Kaltschmitt* et al.*, 2009]*

Presently, a significant share of Austrian straw is either used for animal farming or left on the field to improve soil quality and replace mineral fertilizer [Kalt *et al.* , 2010]. To estimate the potential, it was therefore assumed that 20% wheat and maize straw are available for energy recovery. The resulting straw potential in Austria sums up to some 850 kt/y. In contrast to woody biomass, it is not necessary to distinguish between the different types of straw. A comparison of experimental results showed that they are very similar in composition [Lee *et al.* , 2007] and in their behavior in the process [Lloyd & Wyman, 2005, Aden, 2008, Ballesteros *et al.* , 2006, Linde *et al.* , 2008]. Therefore the potential can be summed up and henceforth the generic term **straw**[4] will be used.

In general it is not planned to provide additional land for biofuel production in Austria. Hence, the biomass potentials indicated here do include only biomass resources presently available in Austria. For that reason no land use change effects [Searchinger *et al.*, 2008] have to be considered when assessing the environmental impact of the technology.

### 2.1.2 BIOMASS COMPOSITION

As outlined in section 2.1.1, spruce and straw are the most abundant types of lignocellulosic biomass in Austria. When converting these types of biomass to ethanol, the composition, particularly the content of carbohydrates that can be fermented to ethanol, is of great importance. In Table 5 the composition of spruce and straw are summarized together with the theoretical ethanol yield that can be obtained assuming 100% conversion[5].

As can be seen, for both types of biomass the carbohydrates content amounts to some 65% of the dry matter. However, the respective amounts of C5 and C6 carbohydrates in spruce and straw differ considerably. Spruce is mainly made up of C6 carbohydrates whereas straw contains significant amounts of C5 carbohydrates. In addition, the amount non-fermentable compounds (lignin, ash and others) is quite different. Straw contains higher amounts of ash, proteins and extractives[6], whereas spruce has a higher lignin content. This difference in composition clearly influences the behavior in the process. However, what holds true for both types of biomass is the fact that a significant share of the lignocellulosic biomass can not be converted to ethanol. As a result, by-product generation (see section 2.4) is a prerequisite to achieve a complete utilization of the biomass. Considering the theoretical yields from Table 5 and the biomass potentials in Table 3 and Table 4, some 450 kt of ethanol (143 kt form spruce and 307 kt from straw) could theoretically be

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[4] *Without specification of the type of straw.*

[5] *Per kg of C6 and C5 carbohydrate in the biomass (i.e. polymeric form) 0.57 and 0.58 kg of ethanol can be obtained theoretically, see sections 2.3.3 and 2.3.4.*

[6] *The latter two are summarized under the category* ***others****.*

produced per year in Austria. However, both the lower conversion yields achieved in reality as well as the economic biomass potential will lower this figure significantly.

*Table 5: Composition of spruce and a generic straw and the resulting theoretical ethanol yields*

| | **Spruce** | **Straw** |
|---|---|---|
| **Water content fresh biomass [w/w%]** | 55% | 10% |
| **Composition of dry biomass [w/w%]** | | |
| Hexosan (C6 carbohydrates) | 58% | 39% |
| Pentosan (C5 carbohydrates) | 8% | 23% |
| Lignin | 28% | 18% |
| Ash | 1% | 7% |
| Others[1] | 5% | 13% |
| **Ethanol yield from C6 carbohydrates** | | |
| [kg Ethanol/kg dry biomass] | 0.33 | 0.22 |
| [l Ethanol/kg dry biomass] | 0.42 | 0.28 |
| **Ethanol yield from C5 carbohydrates** | | |
| [kg Ethanol/kg dry biomass] | 0.05 | 0.13 |
| [l Ethanol/kg dry biomass] | 0.06 | 0.17 |
| **Ethanol yield from C6 & C5 carbohydrates** | | |
| [kg Ethanol/kg dry biomass] | 0.38 | 0.36 |
| [l Ethanol/kg dry biomass] | 0.48 | 0.45 |

*[1] Others include: Plant protein, extractives, acetyl groups, etc. References for straw: [Lee* et al. *, 2007], spruce: [Sassner & Zacchi, 2008, Zhu & Pan, 2010]*

## 2.2 INTRODUCTION TO ETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

Currently, ethanol is commercially produced from grains or sugar cane. In these raw materials the carbohydrates are mainly responsible for energy storage and are consequently relatively easy to access. This easy accessibility is results is relatively simple pre-processing in ethanol production, as can be seen in Fig. 2-1. In sugar cane monomeric sugars are directly available in the plant and can be obtained by mechanical methods (crushing, pressing) [W.M. Ingledew & Kluhsies, 2009]. In addition to mechanical processing (milling), starchy materials require comparatively simple enzymatic steps for starch liquefaction and hydrolysis to gain monomeric sugars [W.M. Ingledew & Kluhsies, 2009].

In contrast to starch and monomeric sugar from cane, carbohydrates in lignocellulosic feedstock fulfill structural purposes. To do so, the polysaccharides cellulose and hemicellulose form a bio-composite with the phenolic polymer lignin (see Fig. 2-2). This composite gives the plants stem stability (cellulose, lignin) as well as flexibility (hemicellulose) [Olsson *et al.* , 2005]. For ethanol production, however this bio-composite of lignocellulosic material poses a challenge because the sugar monomers necessary for ethanol fermentation are embedded in this complex structure and chemically bound as polymers.

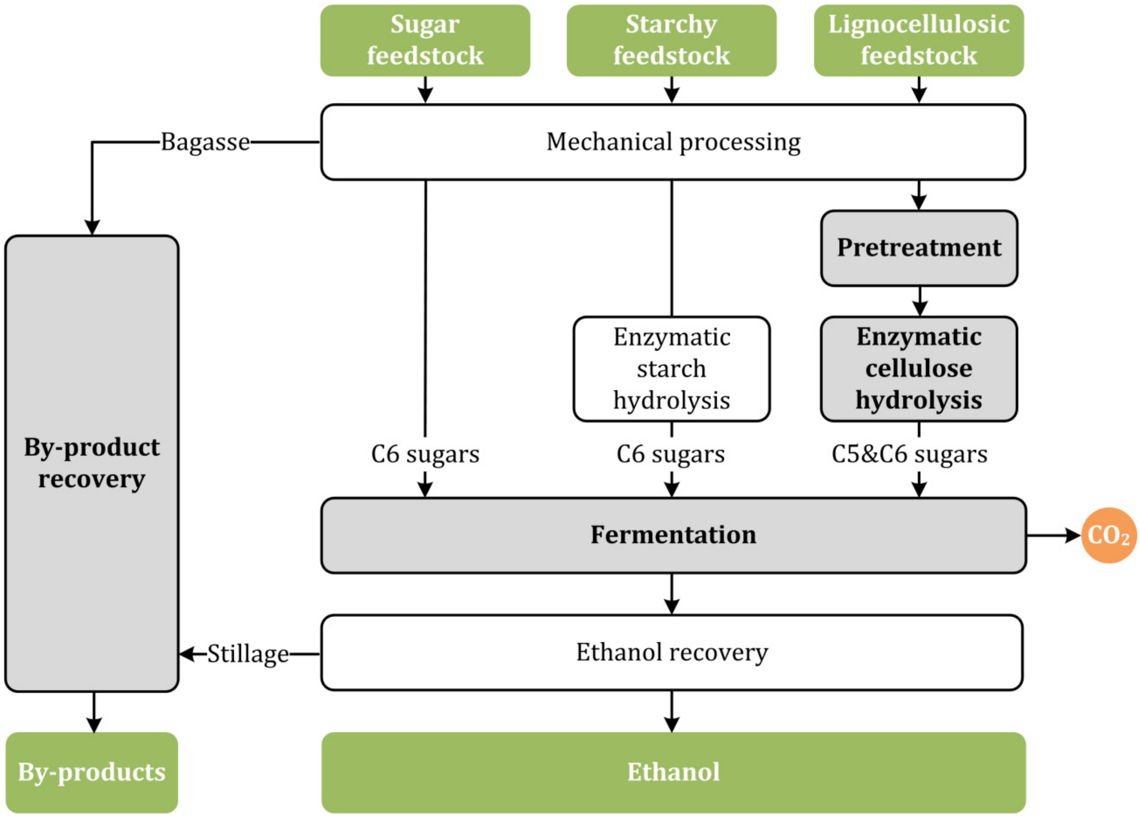

*Fig. 2-1: Biochemical ethanol production from conventional (sugar and starchy) and lignocellulosic feedstock*

To obtain the sugar monomers it is thus necessary to: i) free the polysaccharides from the complex bond and ii) hydrolyze the polysaccharides to monomeric sugars [Mosier *et al.* , 2005]. In principle, these steps can be carried using either acid (dilute or concentrated) or enzymes in combination with a pretreatment step [Fan *et al.* , 1987, Sheehan, 2001]. Today it is widely agreed that the enzymatic route is most promising [Wooley *et al.* , 1999, Sheehan, 2001, Hahn-Hägerdal *et al.* , 2006]. This agreement is based on the expectable improvements in enzyme technology as well as on the high operating and investment cost in acid processes (cost of chemicals, disposal of wastes, stainless steel equipment). As a consequence most R&D is concentrated on the enzymatic processes [iea, 2010] and also in this work, only the enzymatic conversion of lignocellulosic biomass is considered (see also Fig. 2-1).

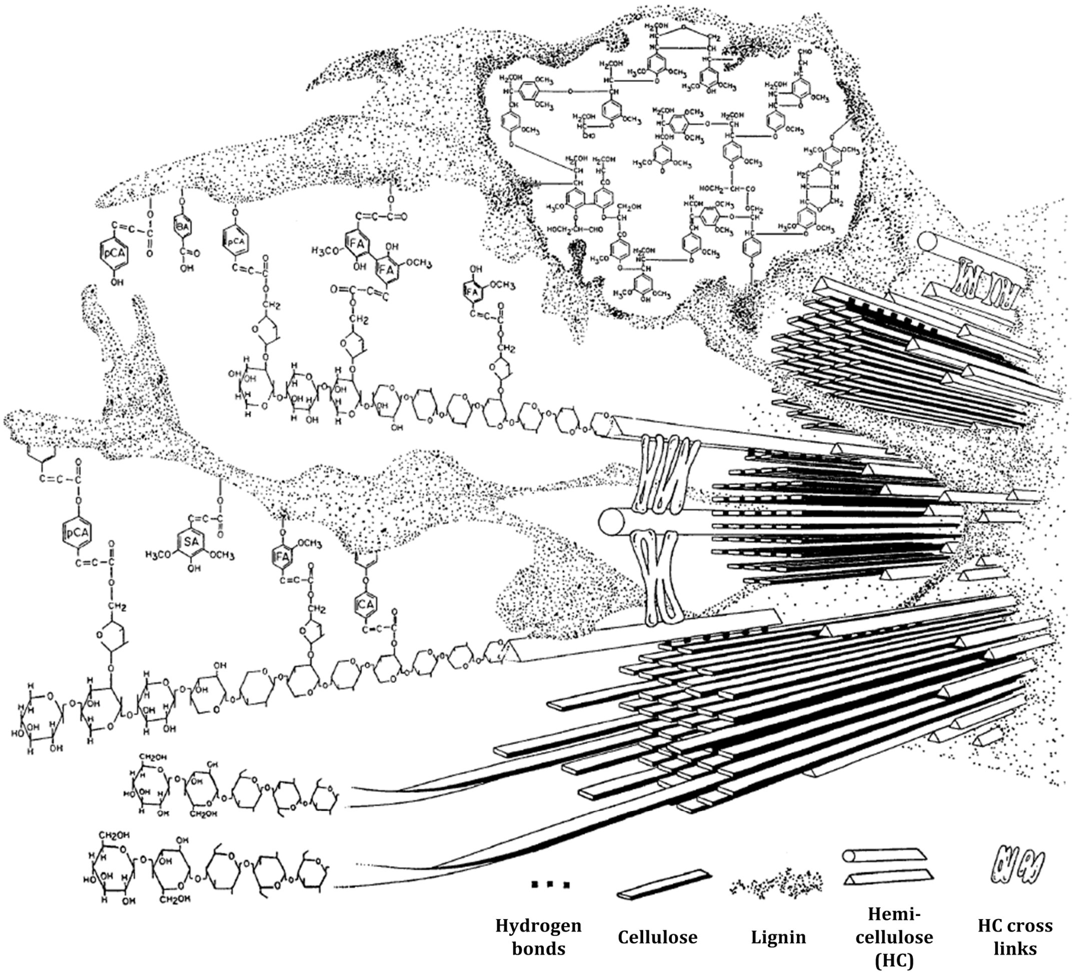

*Fig. 2-2: Artistic representation of secondary cell wall structure of a generalized grass. Cellulose microfibrils and hemicellulose chains are embedded in lignin. Source: [Bidlack* et al.*, 1992]*

Once the monomeric sugars are obtained from hydrolysis of lignocellulosic biomass they can be readily fermented to ethanol by microorganisms. In conventional ethanol production **baker's yeast** (*Saccharomyces cerevisiae*) is used to ferment starch hydrolysates or cane sugar [W.M. Ingledew & Kluhsies, 2009]. *S. cerevisiae* has become the industrial standard because of its various favorable characteristics However, when lignocellulosic hydrolysates are used for fermentation, two major problems arise. First, *S. cerevisiae* lacks the capability to utilize C5 sugars originating from the hemicellulose fraction [Hahn-Hägerdal *et al.* , 2007a] and second, lignocellulosic hydrolysates contain not only sugars but also various inhibiting compounds that mainly originate from pretreatment [Olsson & Hahn-Hägerdal, 1996]. In addition to successful pretreatment and hydrolysis technologies, the development of efficient fermentation is thus crucial for lignocellulosic ethanol to succeed.

After successful fermentation, ethanol has to be recovered from the lignocellulosic beer and purified. Compared to conventional ethanol production two major challenges arise in the product recovery from these beers. First, large amounts of insoluble solids are contained in lignocellulosic beer and second, the ethanol concentration is lower. Nonetheless, as in conventional ethanol production, multicolumn distillation and molecular sieve adsorption are the first choice for product recovery and purification [Aden *et al.* , 2002, Sassner, 2007], even though a wide variety of alternative technologies is available [Vane, 2008, Huang *et al.* , 2008].

In ethanol production from grains, the bottom product from distillation (stillage) contains mainly water but also all non-fermentable components and yeast. After further processing, the solid organic residues are usually sold as an animal feed with high nutritional value [W.M. Ingledew & Kluhsies, 2009]. Generating more than 20% of the total income of the ethanol plant [Kwiatkowski *et al.* , 2006] this by-product is vital for the economic performance of starch based ethanol. Similarly, the economics of ethanol produced from sugarcane can be improved via incomes from fermentation residues [Quintero *et al.* , 2008]. Moreover in the sugarcane process, heat and electricity exceeding the process needs are generated from the bagasse[7] leading to further substantial cost savings through by-product generation. For lignocellulosic ethanol effective by-product generation is even more important. Due its heterogeneous composition and the large amounts of non-fermentable compounds, by-product generation is a key-strategy to make lignocellulosic ethanol a economically competitive (see also ***Paper V***).

## 2.3 UNIT OPERATIONS FOR ETHANOL FROM LIGNOCELLULOSIC BIOMASS

In this section the unit operations for ethanol production from lignocellulosic materials are described. For each unit a general technology description is followed by a section that contains the relevant process parameters. These parameters were obtained from a detailed review of the literature and are used as a basis for flowsheet modeling. The actual values that were applied in flowsheet simulations are summarized in Appendix B. In this context it is important to note that the values that were set in flowsheet simulations generally resemble the best experimental values obtained in lab- or pilotscale. The results of flowsheet simulations can thus be considered as benchmarks for the technology.

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[7] *The fibrous residues from sugar extraction from sugar cane.*

### 2.3.1 *MECHANICAL PROCESSING OF LIGNOCELLULOSIC BIOMASS – SIZE REDUCTION*

Once in the conversion facility, the reduction of biomass size is the first unit operation[8]. In ethanol production from lignocellulosic biomass size reduction is a pre-processing operation that has the goal to enable biomass handling and to increase the surface for pretreatment and hydrolysis [Igathinathane *et al.* , 2008]. For these further processing steps good properties have to be attained while the energy consumption must be kept low.

#### 2.3.1.1 Technology

For the different types of biomass (herbaceous vs. woody) there are various technologies for size reduction available including **chipping**, **crushing**, **shredding**, **cutting**, **milling**, **grinding**. For a given biomass the technologies differ in operating principle, the allowable particle sizes prior to and after size reduction as well as in the specific energy consumption. In general, more energy is required for finer particle sizes and hence for bioenergy production the choice is limited to those technologies that produce rather coarse particles. In particular, grinding of biomass to a very fine powder is not feasible for sole bioenergy production [Galbe & Zacchi, 2007]. The required particle size for lignocellulosic ethanol production depends on the type of biomass and on the subsequent processing steps, especially the pretreatment technology.

#### 2.3.1.2 Process Parameters

**Straw** usually reaches the conversion plant in baled form [Aden *et al.* , 2002]. When a hydrothermal pretreatment[9] is employed particle sizes have to be reduced to a length of 50–100 mm [Larsen *et al.* , 2008]. These lengths are sufficient for an effective pretreatment and can be obtained using knife mills [Bitra *et al.* , 2009] or shredders [Aden *et al.* , 2002]. For a pilot scale **knife mill** the specific electrical energy consumption was experimentally determined for various sorts of baled herbaceous biomass [Bitra *et al.* , 2009]. The requirements to produce corn stover and wheat straw particles (≤25 mm) were determined with 32 and 38 kJ/kg of fresh biomass; with about 41 kJ/kg, the specific energy consumption of large scale **shredding** is almost identical [Aden *et al.* , 2002].

In contrast to straw, **softwood** is either received as logs or as wood chips, depending on the harvesting technology [nwh, 2012]. When logs are received **chipping** takes places at the bioethanol facility and is sufficient for acid impregnated steam pretreatment. Experiments showed that coarse softwood chips with sizes of (5–6)*(30–45)*(30–45) mm [Monavari *et al.* , 2009] or 50*50 mm [Cullis *et al.* , 2004] allow for effective pretreatment and hydrolysis. Smaller chip sizes do not result in higher sugar yields and consequently no

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[8] *Depending on the type and quality of the feedstock unwrapping of bales, washing and removal of dirt and stones may be necessary previously.*

[9] *Hydrothermal pretreatment is a generic term for all pretreatments employing water (in liquid or gaseous state) as major reactant. See also section 2.3.2.*

size reduction beyond coarse chipping is necessary for softwood and acid impregnated steam pretreatment. The specific energy requirement (electrical energy or diesel fuel) for chipping softwood at the conversion plant range from 28 to 55 kJ/kg of fresh biomass [Wihersaari, 2005, Eriksson & Gustavsson, 2008], which is the same range as the specific energy consumption for size reduction of straw. Moreover, for woody biomass there exists the option to perform further size reduction (disk milling) after a sulfite pretreatment [Zhu *et al.* , 2009]. However, when acid impregnated steam pretreatment is employed, coarse chipping is sufficient.

Summing up, for both types of biomass suitable size reduction technologies are available. Good pretreatment and hydrolysis results can be obtained while the size reduction energy consumption can be kept below 1% of the energy contained in the biomass. Data that was applied in flowsheet simulations can be found in Appendix B.

### *2.3.2 PRETREATMENT*

When the particle size is adjusted, the biomass can be subjected to pretreatment. Pretreatment is a key step in ethanol production from lignocellulosic feedstock and has the goal to optimally prepare the biomass for enzymatic hydrolysis. To do so the pretreatment must break up the compound structure of lignocellulosic biomass, as schematized in Fig. 2-3. After an effective pretreatment the polysaccharides should be found in a form that can be hydrolyzed rapidly and with high yields. This is the case when the pretreatment technology succeeds to cause some or all of the following effects [Mosier *et al.* , 2005]: i) increase the accessible surface area, ii) decrystallize cellulose, iii) remove hemicellulose, iv) remove lignin or v) alter lignin structure.

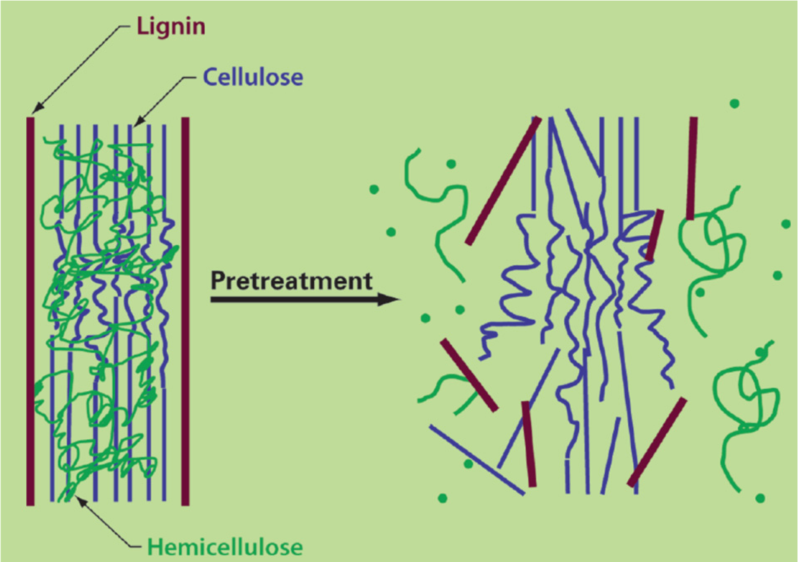

*Fig. 2-3: The desired effects of pretreatment. Source [usd, 2006]*

At the same time, the recovery of all carbohydrates should be as high as possible and the formation of sugar and lignin degradation products should be avoided [Galbe & Zacchi, 2007]. These degradation products can hinder or inhibit the hydrolysis and fermentation; when their level is too high an additional detoxification step[10] can become necessary. Moreover, an ideal pretreatment should result in a high solids and sugar concentration, have a low energy and chemical demand and have low capital and operational cost [Galbe & Zacchi, 2007].

#### 2.3.2.1 Technology

There exists a wide range of pretreatment technologies differing in operating equipment, pretreatment conditions (time, temperature and pressure, chemicals, mechanical stress,…) and mode of action. The classification of the technologies can be based upon the mode of action distinguishing between **i) biological**, **ii) physical**, **iii) chemical** and **iv) physico-chemical** methods [Alvira *et al.* , 2010, Galbe & Zacchi, 2007]. However, oftentimes combinations of these methods are used or the categorization of the technologies is not clear.

In **biological pretreatment** the microbial capability to selectively degrade lignin and hemicellulose is exploited. This degradation is caused by enzymes (laccases and peroxidases) which are produced by white or soft rot fungi [Kumar *et al.* , 2009]. Compared to all other pretreatment methods biological pretreatment has the advantage that the energy requirement is very low and that no sophisticated equipment is required. However, during microbial degradation some of the biomass is consumed and therefore lost for ethanol (polysaccharides) or by-product (lignin) generation. Most importantly, as of today the rate of biological lignin degradation is still too slow (several weeks) for this type of pretreatment to be economically feasible [Galbe & Zacchi, 2007, Alvira *et al.* , 2010].

**Physical methods** are those methods, where mainly physical forces act. **Mechanical comminution** of coarse particles (see section 2.3.1) to finer particle sizes using mills or grinders one purely physical pretreatment. The reduction of particle size increases the specific surface and reduces the degree of polymerization [Alvira *et al.* , 2010]. However, mechanical comminution fails to remove hemicellulose and lignin and most importantly the energy consumption is in general too high for bio-energy production [Galbe & Zacchi, 2007]. **Extrusion** is another physical method, where thermal and chemical effects take place in addition to the reduction of particle size [Alvira *et al.* , 2010]. For biogas production, extrusion is a very attractive pretreatment option that results in a significant increase in biogas yield and overall performance [Hjorth *et al.* , 2011]. Consequently

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[10] *Additional detoxification steps should be avoided. They result in the need for additional equipment, utilities and chemicals, all affecting the production economics negatively.*

extrusion is already widely applied at commercial scale biogas production [leh, 2012]. For ethanol production however, extrusion has not achieved this status yet. **Irradiation with gamma rays** or **microwaves** are further rather exotic physical pretreatment methods. They usually consume a lot of energy and are far too expensive to be feasible for bio-energy production [Galbe & Zacchi, 2007].

As the name implies, **chemical methods** make use of chemicals to pretreat lignocellulosic biomass. Typically elevated temperatures (up to 220 °C) are employed to increase the reaction rate in pretreatment. Chemical methods can be further categorized into: **i) alkali ii) acid iii) oxidizing iv) organosolv** and **v) ionic liquid** pretreatments; oftentimes combinations of the corresponding chemicals are employed. **Alkaline** chemicals like sodium, potassium, calcium or ammonium hydroxide cause a swelling of the pores, solubilize lignin and to a minor extent hemicellulose and break the bonds between lignin and carbohydrates. Thus alkali pretreatment is more effective on substrates with low lignin content (herbaceous biomass) [Galbe & Zacchi, 2007]. The major effect of dilute **acid** pretreatment is the hydrolysis of hemicellulose to sugar monomers and oligomers. Thereby, cellulose becomes accessible for enzymatic attack. Dilute acid pretreatment has been investigated with sulfuric, hydrochloric, phosphoric and nitric acid [Alvira *et al.* , 2010], however sulfuric acid is the most promising one due to its low cost and the good results obtained. A major disadvantage of dilute acid pretreatment is the formation of undesired by-products. **Oxidizing** agents like air, oxygen, hydrogen peroxide or ozone have also been tested for the pretreatment of lignocellulosic biomass. The main effect of these agents is the oxidation and dissolution of lignin [Alvira *et al.* , 2010, Galbe & Zacchi, 2007, Taherzadeh & Karimi, 2008],]. This effect can be enhanced through the combination with bases. **Organosolv** pretreatments employ organic solvents including methanol, ethanol, organic acids and acetone to solubilize lignin [Zhao *et al.* , 2009]. Usually these chemicals are used in combination with water, sometimes also with other chemicals (acids, bases, oxidizing agents). In organosolv pretreatments the lignin fraction can be found mainly dissolved in the liquid phase, whereas cellulose prevails as an insoluble solid. This is why these methods are considered as an attractive option for lignin platform bio-refinery concepts [Zhao *et al.* , 2009]. However, as of today the market for lignin chemicals is very limited which poses a significant problem for these bio-refinery concepts. Recently, **ionic liquids** have received a lot of attention. This is due to their capability to dissolve lignocellulosic biomass along with other interesting features for biorefinery applications[11]. However, dissolution experiments have mainly been conducted on model substrates and many questions remain to be answered before ionic liquids can be utilized in industrial processes [Alvira *et al.* , 2010].

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[11] *Chemical and thermal stability, non-flammability, low vapor pressure, the tendency to stay in the liquid phase over a wide temperature range [Alvira* et al.*, 2010].*

**Physico-chemical** includes methods that are a combination of, or in between physical and chemical methods [Galbe & Zacchi, 2007]. The best studied methods fall into this category. **Ammonia fiber explosion** (AFEX) is an alkaline method in which biomass is treated with anhydrous ammonia (1–2 g per g biomass) at moderate temperatures (60–100 °C) but elevated pressures (15–20 bar) [Galbe & Zacchi, 2007, Alvira *et al.* , 2010, Elander *et al.* , 2009]. After a relatively short period (<30 min) the pressure is released rapidly and ammonia evaporates and can be recycled. AFEX causes a swelling and disruption of the biomass, a partial hemicellulose hydrolysis without formation of inhibitors but only very limited solution of biomass. Major disadvantages of AFEX are the potentially costly ammonia recovery system [Alvira *et al.* , 2010] and its limited effects on woody biomass [Galbe & Zacchi, 2007]. **Ammonia recycle percolation** (ARP) is another pretreatment method employing ammonia, however in aqueous solution (10–15 wt%) and at higher temperatures (150–170 °C). In ARP ammonia is percolated through the biomass and thereafter recycled. ARP pretreatment shows similar effects as AFEX, however with higher dissolution of hemicellulose [Galbe & Zacchi, 2007, Alvira *et al.* , 2010, Elander *et al.* , 2009]. **$CO_2$ explosion** is an interesting option for pretreatment because the pretreatment chemical can be obtained as a by-product of ethanol fermentation in a very pure form(see section 2.4). In $CO_2$ explosion, biomass is brought in contact with supercritical $CO_2$ which is capable to remove lignin from the lignocellulosic compound. An explosive pressure release causes a disruption of the biomass which increases the accessible surface area. Through the gaseous state of $CO_2$ at ambient conditions, $CO_2$ separation is very simple, however sugar yields are lower compared to other methods and the very high pressures necessary result in high investment cost [Alvira *et al.* , 2010]. Steam explosion or **steam pretreatment** is definitely the most studied and used pretreatment method for ethanol production from lignocellulosic biomass. Biomass is treated with high-pressure saturated steam for several minutes. Thereafter the pressure is released rapidly causing a disruption of the material. The main effect however is the hydrolysis of hemicellulose to sugar mono- and oligomers. The dissolution of cellulose and lignin is small but the lignin structure is altered. Steam pretreatment significantly increases the cellulose surface which enhances enzymatic digestibility [Alvira *et al.* , 2010]. Steam pretreatment is often performed with addition of small amounts of an acid catalyst which increases the hydrolysis of hemicellulose. When this is the case, the term **dilute acid** hydrolysis or pretreatment [Aden *et al.* , 2002] is used interchangeably. For woody biomass it is advantageous to perform steam pretreatment in two steps [Söderström, 2004]. **Liquid hot water pretreatment** is similar to steam pretreatment, however, i) evaporation is suppressed by heating water and biomass in a restricted volume, ii) the solids loading is lower and iii) no rapid expansion is performed [Alvira *et al.* , 2010]. Compared to steam pretreatment in liquid hot water pretreatment the hemicellulose hydrolysis yields more sugar oligomers. All methods using exclusively water (either liquid or as steam) for pretreatment, can be summarized by the term **hydrothermal pretreatment**.

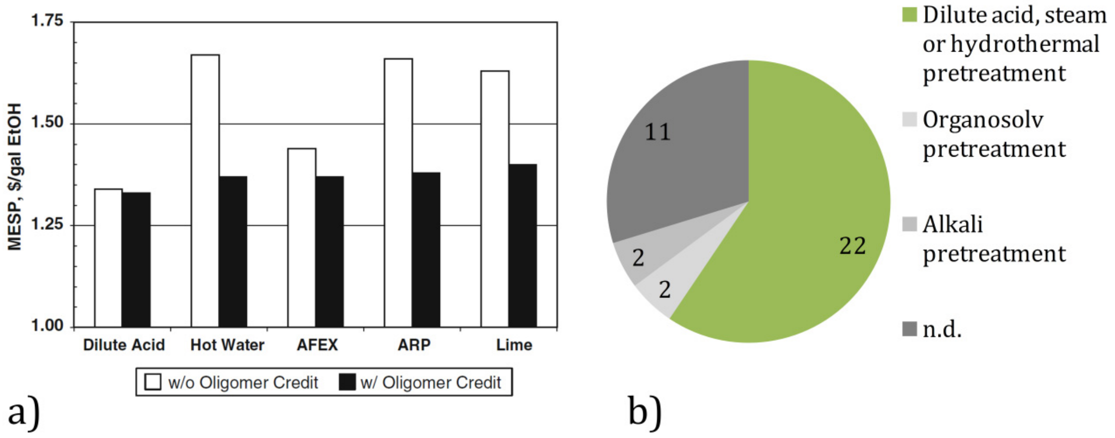

*Fig. 2-4: Maturity of pretreatment technologies. a) Minimum ethanol selling price (MESP) for ethanol production from corn stover with different pretreatment technologies. Data is taken from the CAFI study [Elander* et al. *, 2009]. b) Pretreatment technologies applied in worldwide pilot- and demo-plants. Hydrothermal pretreatment is a generic term for methods employing exclusively liquid water or steam. Alkali pretreatment includes AFEX, ARP and Lime (Calcium hydroxide) pretreatment. n.d. not defined. Source: [iea, 2010]*

At present **acid catalyzed steam pretreatment** or **dilute acid hydrolysis** is considered the most mature technology. This is on the one hand reflected in the lowest production cost (see **Dilute Acid** in Fig. 2-4 a) and on the other hand in the incidence of use in worldwide pilot-, demonstration and commercial projects (see Fig. 2-4 b). Moreover, only for this pretreatment technology, extensive experimental data is available. Consequently steam pretreatment with addition of $SO_2$ will be the exclusive pretreatment technology considered in this work.

### 2.3.2.2 Process Parameters

In this subsection literature data for acid catalyzed steam pretreatment is presented. In steam pretreatment shredded straw or chipped softwood is moistened to reach a water content of 55–65 w/w%[12]. After addition of small amounts of acid (less than 3 w/w% of water in biomass, $SO_2$ or $H_2SO_4$) the mixture is brought to temperatures of 160–240 °C using saturated high pressure steam. Direct injection of steam can be applied solely or can be comined with indirect heating. Biomass is held at these temperatures for up to ten minutes. The steaming results in a hydrolysis of mainly hemicellulose but also of cellulose (see Equations (1) and (2)) [Galbe & Zacchi, 2007]. In addition to these hydrolysis reactions, unwanted degradation of sugar monomers to furfural and hydroxymethylfurfural (HMF) can take place (see Equations (3) and (4)). These

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[12] *Fresh softwood contains approx. 50 w/w% water and does not have to be moistened.*

potentially inhibiting compounds can be further degraded to levulinic and formic acid. Moreover during hydrolysis, acetyl groups from hemicellulose are released to form acetic acid (Equation (5)) and lignin is partially solubilized [Larsson *et al.* , 1999, Palmqvist & Hahn-Hägerdal, 2000].

$$(C_5H_8O_4)_n + n\,H_2O \rightarrow n\,C_5H_{10}O_5$$ *(1) Hydrolysis of C5 carbohydrates xylan and arabinan (hemicellulose)*

$$(C_5H_8O_4)_n + n\,H_2O \rightarrow n\,C_6H_{12}O_{12}$$ *(2) Hydrolysis of C6 carbohydrates glucan (cellulose), mannan, galactan (hemicellulose)*

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3\,H_2O$$ *(3) Degradation of pentoses to furfural*

$$C_6H_{10}O_5 \rightarrow C_5H_4O_2 + 3\,H_2O$$ *(4) Degradation of hexoses to hydroxymethylfurfural (HMF)*

$$CH_3COR + H_2O \rightarrow CH_3COOH + RH$$ *(5) Release of acetic acid from acetyl groups in hemicellulose (R)*

The extent to which these reactions occur depends on the type of biomass as well as on the pretreatment conditions (time, temperature, amount of catalyst). Finding the optimal pretreatment conditions, at which an effective hydrolysis of hemicellulose is achieved while the formation of inhibitors is kept as low as possible, has been the goal of extensive research work. Experimental data for optimal pretreatment conditions are listed in Table 6.

*Table 6: Optimal conditions for steam pretreatment of straw and softwood with $H_2SO_4$ or $SO_2$ catalyst*

| **Biomass** | **Time** | **Temperature** | **Catalyst loading** | **References** |
|---|---|---|---|---|
| Straw[1] | 2 – 10 min | 180 – 190 °C | 0.2 – 3 w/w%[2] | 1 |
| Softwood, step 1 | 5 min | 180 – 190 °C | 1 – 3 w/w%[2] | 2 |
| Softwood, step 2 | 5 min | 210 – 220 °C | 2.5 – 3 w/w%[2] | 2 |

[1] *Wheat straw or corn stover,* [2] *Based on the water content in the biomass. References: 1: [Lloyd & Wyman, 2005, Öhgren* et al.*, 2005, Aden, 2008, Linde* et al.*, 2008], 2: [Wingren* et al.*, 2004, Monavari* et al.*, 2009, Nguyen* et al.*, 2000, Söderström* et al.*, 2002]*

Because straw is less recalcitrant, milder pretreatment conditions (lower temperature, less catalyst) are applied. On the other hand, softwood is more recalcitrant and requires harsher conditions [Galbe & Zacchi, 2007]. However, too harsh conditions result in excessive inhibitor formation. To prevent this inhibitor formation two step pretreatment has been successfully applied for steam pretreatment of softwood [Wingren *et al.* , 2004, Monavari *et al.* , 2009, Nguyen *et al.* , 2000, Söderström *et al.* , 2002]. In a first, milder pretreatment step hemicellulose is hydrolyzed and soluble mono- and oligomers are recovered. In the second, harsher step, hemicellulose hydrolysis is completed and cellulose digestibility is increased.

Fig. 2-5 displays experimental results for acid catalyzed steam pretreatment of straw (corn stover and wheat straw) using the operating conditions from Table 6. The major fraction (approx. 90%) of glucan (cellulose) remains as an insoluble polymer, whereas 5–10% of glucan are solubilized to mono- or oligomers (see equation (2)) and less than 5% are lost or converted to HMF (see equation (4)). Compared to cellulose, hemicellulose (xylan[13]) is solubilized and degraded more easily. With operating conditions from Table 6, only 5–30% remain insoluble, whereas the major fraction (60–80%) is hydrolyzed to mono- or oligomers (see equation (1)) and less than 10% are degraded to furfural (equation(3)) or lost.

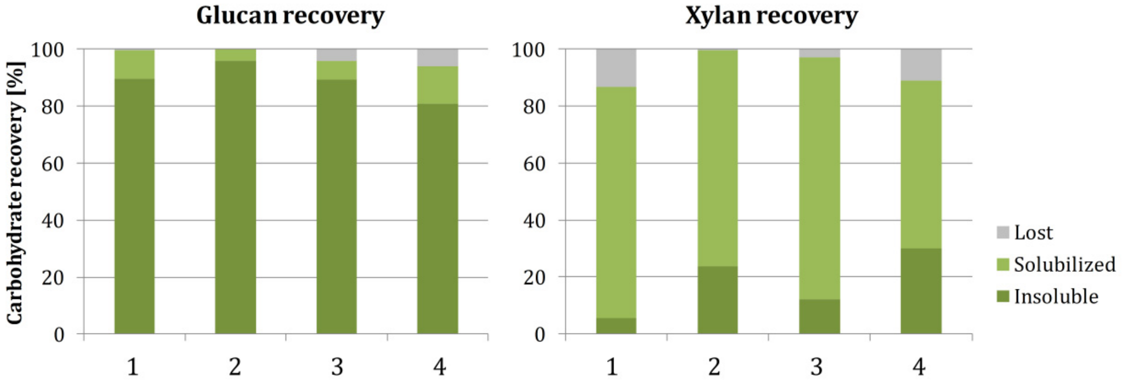

*Fig. 2-5: Acid catalyzed (SO2 or H2SO4) steam pretreatment of corn stover and wheat straw. Carbohydrate recovery for glucan (cellulose) and xylan (hemicellulose.) is shown. Pretreatment conditions are listed in Table 6. References: 1: [*Aden, 2008*] (corn stover), 2: [*Linde *et al.* , 2008*] (wheat straw), 3: [*Lloyd & Wyman, 2005*] (corn stover), 4: [*Öhgren *et al.* , 2005*] (corn stover).*

Experimental results for combined carbohydrate recovery[14] in two step acid catalyzed steam pretreatment of softwood are shown in Fig. 2-6. Compared to straw treated with single step steam pretreatment, higher fractions of cellulose and hemicellulose carbohydrates, (glucan and mannan) are hydrolyzed, which can be explained by the harsher pretreatment conditions (see Table 6). Only 30–70% of glucan (cellulose) remain unconverted as an insoluble polymer, whereas 20–60% are hydrolyzed to mono- or oligomers (see equation (2)). Mannan (hemicellulose[15]) is almost completely converted to sugar mono–and oligomers (see equation (2)[16]). Certainly due to the harsh pretreatment

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[13] *The C5 polymer xylan is the main constituent of hemicellulose in straw. In experimental studies, complete recovery data is usually only reported for xylan, but not for the other constituents of hemicellulose in straw.*

[14] *i.e. the recovery after two steps.*

[15] *The C6 polymer mannan is the main constituent of hemicellulose in softwood. In experiments, recovery data is usually only reported for mannan, but not for the other constituents of hemicellulose in softwood.*

[16] *Mannan is a C6 sugar, which is why equation (2) applies.*

conditions sugar losses are also higher in the two step pretreatment of softwood. Glucan losses account for 2–10% and mannan losses for 10–15% (see equation (4)).

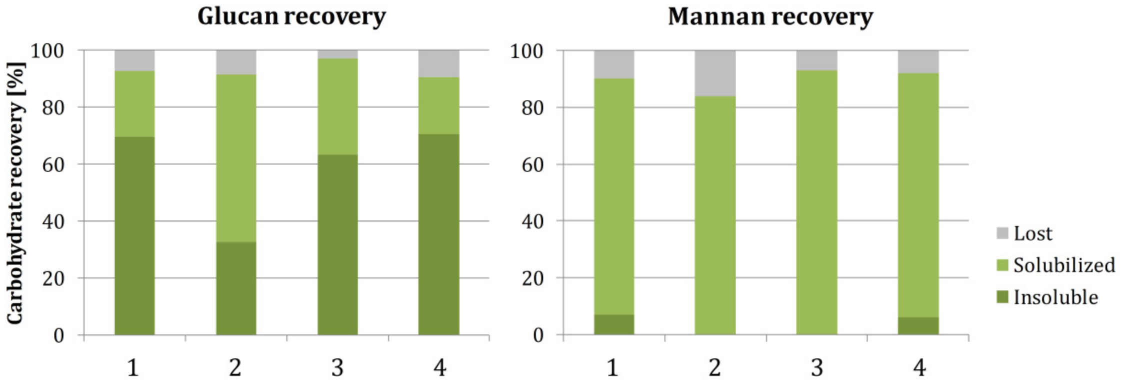

*Fig. 2-6: Two step acid catalyzed ($SO_2$ or $H_2SO_4$) steam pretreatment of softwood. Carbohydrate recovery for glucan (cellulose) and mannan (hemicellulose.) is shown. Pretreatment conditions are listed in Table 6. References: 1: [Monavari* et al. *, 2009], 2: [Nguyen* et al. *, 2000], 3: [Söderström* et al. *, 2002] 4: [Wingren* et al. *, 2004]*

After a few minutes residence time, during which the chemical conversion of biomass takes place, the biomass is released explosively through a valve. This flashing to atmospheric conditions causes a disruption of the material and a separation of phases. The vaporous phase contains mainly water vapor, but also parts of the volatile by- and degradation products formic acid, acetic acid, furfural, HMF and levulinic acid. The heat released by condensation of the vaporous phase can be used to heat other process parts (see section 3.3). To obtain higher quality heat, flashing at two steps can be beneficial [Wingren *et al.* , 2003]. Heat recovery from steam pretreatment is discussed in more detail in section 3.3 and in ***Paper II***. Data that was applied in flowsheet simulations can be found in Appendix B.

### 2.3.2.3 Subsequent processing steps

The condensed phase obtained from flashing is an aqueous mixture of insoluble (mainly cellulose and lignin) and soluble solids (sugar mono- and oligomers, mainly from hemicellulose, plant proteins, extractives, etc.) and will be henceforward referred to as **slurry**. The slurry also contains the acid catalyst ($SO_2$), which is oxidized to $SO_4^{2-}$ during the pretreatment [Bari *et al.* , 2007]. Before the slurry can be hydrolyzed and fermented to ethanol, the acidic biomass must be neutralized or even detoxified (conditioned[17]). As far as neutralization is concerned, some aspects have to be considered in addition to the acid

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[17] *In the literature the term conditioning refers to „methods developed to treat hydrolysate to reduce toxicity and make the sugars more accessible to fermentation" [Pienkos & Zhang, 2009].*

catalyst from pretreatment. On the one hand acetyl groups are released from hemicellulose and form acetic acid. This acetic acid that is released from biomass causes an increase in the demand of neutralizing agent. On the other hand, inorganic compounds in the biomass (ash) act as a buffer, whose buffering capacity has to be determined experimentally [Lloyd & Wyman, 2005, Weiss *et al.* , 2010]. In general, the buffering capacity of ash does not suffice and neutralization to neutral or slightly acidic conditions[18] is necessary. Thereto NaOH, $Ca(OH)_2$, KOH or ($NH_4OH$) can be applied [Pienkos & Zhang, 2009].

A detoxification becomes necessary, when the microorganism used for fermentation can not tolerate the type and amount of inhibitors formed during fermentation. There are several methods for detoxification available of lignocellulosic hydrolysates (biological, physical, chemical)[19] [Pienkos & Zhang, 2009] however, chemical methods are most widely suggested and used. One of the first and best studied methods for detoxification is **overliming**, where lime ($Ca(OH)_2$) is used to raise the pH of the hydrolysate to values above 10. Thereafter the pH is set back to neutral values using $H_2SO_4$. The solid gypsum ($CaSO_4$) formed has to be removed in a solid/liquid separation step [Aden *et al.* , 2002]. This solid/liquid separation also leads to sugar losses. When **ammonium hydroxide** ($NH_4OH$) is used instead of lime, a solid/liquid separation step can be avoided, because no solids are formed. Since similar fermentability can be achieved using this method, it is considered the better choice for detoxification [Aden, 2008]. In general, however, a detoxification step should be avoided if possible.

### *2.3.3 ENZYMATIC HYDROLYSIS OF PRETREATED BIOMASS*

To goal of pretreatment is to optimally prepare the biomass for enzymatic cellulose hydrolysis, which is achieved by decrystallizing cellulose and freeing it from lignin and hemicellulose. Once this is achieved, enzymes can efficiently hydrolyze cellulose to monomeric glucose, which is subsequently fermented to ethanol. The goal of enzymatic hydrolysis is therefore to convert cellulose and still unreacted hemicellulose to monomeric sugars as completely as possible.

#### 2.3.3.1 Technology

The neutralized slurry obtained from a successful pretreatment contains partly liberated and decrystallized cellulose microfibrils. In enzymatic hydrolysis these cellulose microfibrils are degraded to monomeric sugars via **cellulase** enzymes. These enzymes are highly specific and compared to acid, which could also be used for hydrolysis (see section 2.2), do not form inhibitors [Sun & Cheng, 2002]. In fact, cellulase is not at single enzyme

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[18] *Depending on the microorganism used in fermentation.*

[19] *In physical methods toxic compounds are removed, in chemical and biological methods they are rendered harmless.*

but a system of different types of enzymes whose concerted and synergistic action yields glucose monomers from cellulose. In Fig. 2-7 a scheme of this enzyme system and its mode of action during hydrolysis of cellulose to glucose monomers is shown. Endoglucanases cut cellulose at internal amorphous regions yielding cello-oligosaccharides with varying chain length. Exoglucanases liberate cellobiose (glucose dimers) from the reducing or non-reducing chain end of the cellulose chain. These soluble cellobiose molecules are hydrolyzed to glucose monomers by β-glucosidase [Lynd *et al.* , 2002].

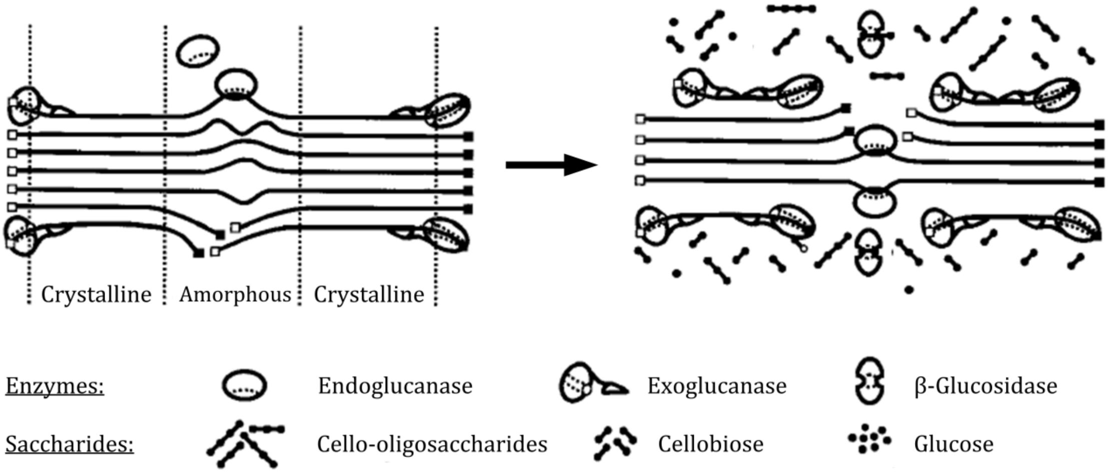

*Fig. 2-7: Scheme of cellulose hydrolysis. Cellulose is cleaved at chain ends and at amporhous regions by exo- and endoglucanases. Cellobiose is cut to glucose monomers by β-glucosidase. Adapted from [Lynd* et al.*, 2002]*

In the ethanol production process a complete conversion of cellulose to glucose should be obtained in the shortest time possible. Moreover, the enzyme loading should be as low as possible and the solids content should be as high as possible. The high solid loading is important for two reasons: On the one hand, increasing the solids loading at otherwise constant parameters corresponds to smaller reactors and downstream equipment which reduces investment cost. On the other hand, a high solid loading result in a higher concentration of sugars and ethanol which reduces the energy consumption of downstream processing[20] [Wingren *et al.* , 2003].

Traditionally, enzyme hydrolysis was performed as a separate step between pretreatment and ethanol fermentation [Lynd *et al.* , 2002]. With this processing strategy termed **separate hydrolysis and fermentation (SHF)** optimal conditions (temperature, pH, ...) can be chosen for each process step [Sun & Cheng, 2002]. Nonetheless, a complete

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[20] *In particular the energy consumption of distillation and evaporation.*

conversion of cellulose to glucose cannot be achieved with SHF because the cellulase enzyme system is inhibited by sugars released during hydrolysis [Sun & Cheng, 2002].

To overcome this so called **end product inhibition** several strategies have been developed. The most prominent strategy is to remove the inhibiting sugars from the hydrolysis broth by fermenting them to ethanol. This processing strategy is termed **simultaneous saccharification and fermentation (SSF)**[21] because cellulose hydrolysis and ethanol fermentation are performed at the same time and in the same reaction vessel [Sun & Cheng, 2002]. In addition to i) avoiding end product inhibition and thereby increasing conversion yields and conversion rate, SSF has the advantages that ii) the enzyme requirements are lower, that iii) requirements for sterile conditions are lower[22] and that iv) less reactor volume is required because a single reactor is used [Sun & Cheng, 2002, Olofsson *et al.* , 2008b]. However, there also are some disadvantages of SSF that have to be taken into account. First, the reaction conditions (temperature, pH, …) for hydrolysis and fermentation cannot be chosen independently, second, the enzymes can be deactivated by ethanol and third, recycling or immobilization of yeast or enzymes becomes infeasible[23] [Sun & Cheng, 2002, Olofsson *et al.* , 2008b].

When conventional yeast (native *S. cerevisiae*) is used for fermentation, C5 sugars are either fermented in a separate process step by a different microorganism (see section 2.3.4) or not converted to ethanol. However, in recent years, a lot of progress has been made towards microorganisms which are capable to co-ferment C6 and C5 sugars to ethanol [Hahn-Hägerdal *et al.* , 2007b]. When such a microorganism is used in a SSF setup the term **simultaneous saccharification and co-fermentation (SSCF)** is used. The challenges of co-fermentation of C6 and C5 sugars in general and particularly in an SSCF setup are discussed in section 2.3.4.

All the processing strategies described above (SHF, SSF, SSCF) share one characteristic: The cellulase enzymes have to be produced in a separate bioprocess with dedicated microorganisms. This dedicated enzyme production can either be performed at the ethanol production facility using part of the pretreated biomass as a substrate (**on-site**) or in a large scale, centralized enzyme factory (**central**, see section 2.3.5). In either case, additional substrate (lactose, cellulose, pretreated biomass) and nutrients are needed for enzyme production. If the ethanol-fermenting microorganisms could produce the enzymes themselves (during their anaerobic, ethanol producing metabolism), higher ethanol yields per unit biomass could be obtained. Moreover an extra reactor for enzyme production and

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[21] *SSF is also used as acronym for* ***solid state fermentation****. Throughout this work it stands for simultaneous saccharification and fermentation.*

[22] *Glucose is immediately removed and ethanol is immediately formed.*

[23] *The insoluble solids entering SSF comprise mainly lignin, cellulose and yeast. The soluble enzymes bind to lignin, forming an insoluble mixture of yeast, enzymes and lignin.*

the associated equipment could be saved, which would reduce investment costs. For this processing strategy, in which one single microorganism is used for enzyme production and fermentation of all sugars, the term **consolidated bioprocessing (CBP)**[24] [Lynd *et al.* , 2002] was suggested. In nature the microorganisms needed for CBP do not exist, which is why intense research efforts are dedicated to the development of these microorganisms. In principle two strategies exist: following the native strategy native cellulotytic microorganisms (fungi and bacteria) are genetically modified to produce ethanol whereas the recombinant strategy aims at developing cellulase expression systems in natural ethanol producers (yeasts and bacteria) [Lynd *et al.* , 2005, Xu *et al.* , 2009]. Even though a lot of progress has been made towards industrial CBP [Jin *et al.* , 2011, Olson *et al.* , 2012], as of today no microorganism is available that can produce sufficient amounts of enzymes to efficiently and quickly hydrolyze cellulose and at the same time produce ethanol with high yield, high selectivity, high titers and high rates [Xu *et al.* , 2009].

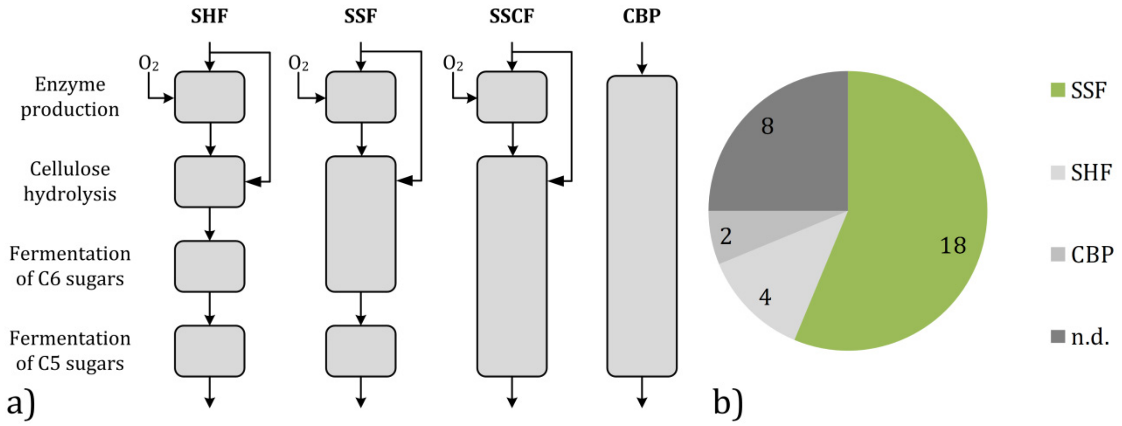

*Fig. 2-8: Processing strategies (SHF, SSF, SSCF and CBP) for bioprocesses in ethanol production. a) A graphical representation. Each box represents a separate bioreactor. From left to right the integration of bioprocessing steps increases. Adapted from [Lynd* et al. *, 2002]. b) Occurrence of hydrolysis technologies applied in worldwide pilot-and demo plants. Source: [iea, 2010]*

When comparing the processing strategies, which are schematized in Fig. 2-8 a, technical maturity and economic aspects have to be considered. SHF and SSF can be considered mature technologies, since they have been successfully proven on pretreated biomass in lab-, pilot- and demonstration scale [Olofsson *et al.* , 2008b, iea, 2010]. On the other hand, CBP has yet to prove its potential [Xu *et al.* , 2009], particularly when it comes to the conversion of natural, pretreated substrates in an industrial environment [Olson *et al.* , 2012]. SSCF can be considered somewhere in between SSF and CBP, as far as maturity is concerned. In this work, only proven technology should be considered, which is why CBP

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[24] *Alternatively the terms* ***direct cellulose fermentation*** *and* ***direct microbial conversion*** *are used.*

will not be dealt with further. When the mature technologies SHF and SSF are compared, SSF outperforms SHF due to higher yields and lower production costs [Wingren *et al.* , 2003, Tomas-Pejo *et al.* , 2008]. As a consequence today, SSF is generally considered to be the most attractive processing technology [Hahn-Hägerdal *et al.* , 2006]. This is also reflected in the incidence of use in worldwide pilot-, demonstration and commercial projects, as shown in Fig. 2-8 b. Here SSF is the dominant processing technology. Hence, SSF and SSCF with *S. cerevisiae* will be the processing technologies considered in this work.

#### 2.3.3.2 Process Parameters

As described above, hydrolysis and fermentation are performed simultaneously in SSF and SSCF and consequently operating conditions cannot be set independently. Moreover, the reaction yields of hydrolysis and fermentation are difficult to measure independently because hydrolysis products (sugars) are directly converted to ethanol, yeast biomass and fermentation by-products. The yield of hydrolysis is thus usually not measured in an SSF or SSCF setup. Therefore, the operating conditions and performance parameters for hydrolysis are described together with fermentation conditions and performance indicators in section 2.3.4. Data that was applied in flowsheet simulations can be found in Appendix B.

### *2.3.4 FERMENTATION OF LIGNOCELLULOSIC HYDROLYSATES*

The fermentation of sugars to ethanol is the product forming reaction in lignocellulosic ethanol production and thus a lot of research has been dedicated to the efficient fermentation of lignocellulose-derived sugars to ethanol. In an effective fermentation all sugars should be converted to ethanol (high yield) without formation of by-products (high selectivity) in the shortest time possible (high productivity). To reduce the energy demand in downstream processing, a high ethanol concentration is also desired. As described in section 2.3.3, fermentation can either be performed simultaneously with hydrolysis (SSF, SSCF and CBP) or as a separate step (SHF), with the simultaneous processing strategy being considered more promising. As described above (see section 2.3.3), SSF and SSCF are the only processing strategies covered in this work. Independent of the processing strategy, the fermentation of lignocellulosic hydrolysates shows some particularities compared to ethanol fermentation from sugar or starch. These will be discussed briefly before listing the most important process parameters.

#### 2.3.4.1 Technology

In ethanol production from conventional feedstock (sugar and starch) baker's yeast *S. cerevisiae* is the industrial standard. This fact can be ascribed to various attractive characteristics of the microorganism, including high yields[25], high productivity, good ethanol tolerance and high robustness[26]. Thanks to these characteristics of *S. cerevisiae* ethanol produced from sugar or starch is today the largest commodity produced by any microorganism in the world [Jacques *et al.* , 2003].

In the fermentation of lignocellulosic hydrolysates two major challenges arise. First, lignocellulosic hydrolysates contain not only sugars but also various potentially inhibiting compounds (see section 2.3.2) whose occurrence depends on both the raw material and the pretreatment applied. Second, the hydrolysates contains not only hexoses (glucose, mannose, galactose) but also pentoses (xylose and arabinose), which can not be fermented by wild-type *S. cerevisiae.* For effective ethanol production from lignocellulosic biomass a microorganisms is thus required that is capable to convert all sugars to ethanol (with high yields and productivities) under the challenging conditions present in lignocellulosic hydrolysates.

Apart from its lacking capability to ferment C5 sugars *S. cerevisiae* is a very attractive candidate. In addition to its qualities exploited in conventional ethanol fermentation, *S. cerevisiae* also shows a high tolerance against the inhibitors in lignocellulosic hydrolysates and is well adapted to industrial use. Due to its utilization in conventional ethanol production it also has clear advantages in an integrated plant utilizing both conventional and lignocellulosic feedstock [Hahn-Hägerdal *et al.* , 2007b]. When softwood with its low content of C5 sugars shall be converted to ethanol (see section 2.1), pentose fermentation may be omitted and wild-type *S. cerevisiae* cultivated on pretreated biomass is an excellent choice. On the other hand, when straw with its high content in C5 sugars is used as a substrate, the lacking capability to ferment C5 sugars is a major disadvantage of *S. cerevisiae*. To overcome this weakness *S. cerevisiae* was genetically modified to express genes for xylose-metabolizing enzymes [Hahn-Hägerdal *et al.* , 2006]. As a result, *S. cerevisiae* strains are available that are capable to simultaneously ferment C5 and C6 sugars in non-detoxified hydrolysates, albeit with slow and incomplete xylose conversion [Hahn-Hägerdal *et al.* , 2007b].

*Zymomonas mobilis*, a facultative anaerobic bacterium, is the main competitor for *S. cerevisiae* [Olofsson *et al.* , 2008b]. The wild type converts glucose with high yields and productivities to ethanol but cannot use galactose, mannose or pentoses. To overcome this disadvantage *Z. mobilis* was successfully modified genetically to co-ferment glucose and xylose [Mohagheghi *et al.* , 2004]. A disadvantage of *Z. mobilis* is its lower inhibitor tolerance which makes a detoxification step (see section 2.3.2) necessary when

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[25] *90–95% of the theoretical yield are reached in conventional ethanol production [Hahn-Hägerdal* et al.*, 2007b].*

[26] *Robustness can be defined as "the persistence of a system's characteristic behavior under perturbations or conditions of uncertainty" [Stelling* et al.*, 2004].*

lignocellulosic hydrolysates are fermented; nonetheless NREL[27] researchers consider *Z. mobilis* the top choice for ethanol production from corn stover [Humbird *et al.* , 2011, Aden *et al.* , 2002].

As shown in Fig. 2-9, in addition to *S. cerevisiae* and *Z. mobilis*, there exists a variety of other microorganisms that can potentially be utilized to ferment lignocellulosic hydrolysates to ethanol. All of them have their particular strengths but also significant shortcomings when it comes to the fermentation of lignocellulosic hydrolysates. Namely these are i) the low inhibitor tolerance (*E. coli, P. stipitis*, anaerobic bacteria), ii) the significant by-product formation (anaerobic bacteria, filamentous fungi), iii) the low productivity (filamentous fungi) or iv) the lacking capacity to produce ethanol (*E. coli*) [Hahn-Hägerdal *et al.* , 2006, Hahn-Hägerdal *et al.* , 2007b].

| | C6 utilization | C5 utilization | Ethanol yield | Inhibitor tolerance | Ethanol tolerance | Productivity |
|---|---|---|---|---|---|---|
| *S. cerevisiae* | + | - | + | + | + | + |
| *Z. mobilis* | +/- | - | + | - | +/- | + |
| *E. coli* | + | + | - | - | - | + |
| *P. stipitis* | + | + | + | - | - | + |
| Anaerobic bacteria | + | + | +/- [1] | - | - | +/- [2] |
| Filamentous fungi | + | + | +/- [1] | + | + | - |

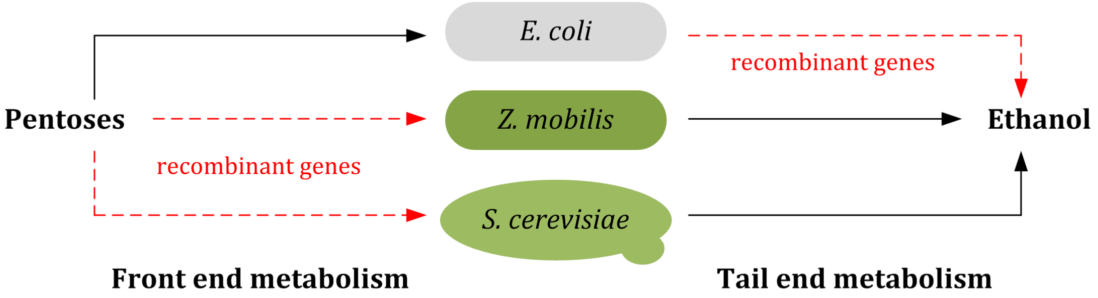

*Fig. 2-9: Microorganisms for ethanol fermentation of lignocellulosic hydrolysates. Top: Strengths and weaknesses of various microorganisms. [1] Anaerobic bacteria and filamentous fungi convert sugars to mixed products (ethanol, acids, hydrogen, …). [2] Productivity strongly varies among species. Adapted from [Hahn-Hägerdal* et al. *, 2007b]. Bottom: Strategies for metabolic engineering for pentose fermentation.Either the front end (as in* Z. mobilis *or* S. cerevisiae*) has to be engineered or the bottom end (as in* E. coli*). Adapted from [Hahn-Hägerdal* et al. *, 2006]*

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[27] *The National Renewable Energy Laboratory (NREL) of the U.S. Departement of Energy is a leading player in lignocellulosic ethanol research.*

To deal with these shortcomings metabolic (genetic) engineering has been applied. As shown in Fig. 2-9, the focus of metabolic engineering has been on pentose utilization and ethanol formation. Either C5 metabolism has been introduced in ethanologen microorganisms (as in *S. cerevisiae* and *Z. mobilis*) or ethanol fermentation has been introduced in naturally C5 fermenting microorganisms (such as *E.coli*) [Hahn-Hägerdal *et al.* , 2006].

Independent of the type of microorganism used, genetic enginnering is necessary when C5 sugars shall be fermented to ethanol. In Austria however, the legal situation regarding the application of geneticall modified organisms (GMOs) in industrial processes is unclear [Reiß, 2009][28]. If GMOs are allowed, strict safety regulations will certainly apply. The use of GMOs and the fermentation of C5 sugars in a potential Austrian lignocellulosic ethanol plant is therefore uncertain.

To summarize, *S. cerevisiae* and *Z. mobilis* are at present the most mature microorganisms for fermentation of lignocellulosic hydrolysates. Due to the avoidance of end-product inhibition in hydrolysis and reduced investment cost, the SSF (SSCF) setup is considered the most attractive processing strategy (see section 2.3.3). To increase the ethanol yield, fermentation of C5 sugars is highly recommended for straw, which is rich in C5 sugars. To that end GMOs are necessary. However, their approval in Austria is unclear. In the following section 2.3.4.2, a literature review of fermentation experiments (SSF and SSCF) carried out on lignocellulosic hydrolysates is presented. These data are supplemented with modeling assumptions other researchers applied in their process calculations [Sassner *et al.* , 2008, Aden *et al.* , 2002].

#### 2.3.4.2 Process parameters

For a given substrate with given pretreatment technology the most important hydrolysis experimental parameters for SSF are: i) the initial amount of water insoluble solid (WIS), ii) the mode of operation[29], iii) the residence time, iv) the enzyme loading[30] v) the temperature and pH. Moreover, in lab scale experiments SSF is performed using either the whole slurry from pretreatment or only the washed solid fraction [Olofsson *et al.* , 2008b]. However, in industrial ethanol production washing the solids is not an option because of the sugar losses and the enormous amounts of water needed.

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[28] *Personal communication with A. Reiß (Vogelbusch Inc.) on 16.07.2009.*

[29] *Shake flasks, batch, fed batch.*

[30] *Enzyme loading is usually given in enzyme **units**/g substrate (cellulose or WIS). One **international unit (IU)** is defined, as the amount of enzyme needed to convert 1 µmol of substrate per minute under standard conditions [Chaplin & Bucke, 1990]. For cellulases the **filter paper unit (FPU)**, as determined in standardized IUPAC assays [Ghose, 1987], is used.*

Obviously, the most important performance parameters are the yields achieved for reactions (2), (6) and (7); but also productivities and final ethanol concentrations are highly relevant in an industrial production process. In addition to these product forming reactions, the undesired byproducts acetic acid and glycerol are formed (see reactions (8) and (9)) [W.M. Ingledew & Kluhsies, 2009, Aden *et al.* , 2002].

| | | |
|---|---|---|
| $(C_6H_{10}O_5)_n + n\,H_2O \rightarrow n\,C_6H_{12}O_6$ | | *(2) Cellulose hydrolysis* |
| $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ | *$\Delta H_R$≈90 kJ/mol C6 sugar [Dellweg, 1987]* | *(6) Ethanol fermentation of C6 sugars monomers* |
| $3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2$ | *$\Delta H_R$≈75 kJ/mol C5 sugar [Wooley & Putsche, 1996]* | *(7) Ethanol fermentation of C5 sugar monomers* |
| $C_6H_{12}O_6 \rightarrow 3\,CH_3COOH$ | | *(8) Formation of acetic acid* |
| $C_6H_{12}O_6 + 2H_2O \rightarrow 2\,C_3H_5(OH)_3 + O_2$ | | *(9) Formation of glycerol* |

In Table 7 experimental parameters for SSF carried out on various types of non-detoxified, pretreated biomass are listed together with parameters applied in process simulations. The sole pretreatment method applied is acid impregnated steam pretreatment (=dilute acid hydrolysis) using $H_2SO_4$ or $SO_2$ as catalyst. As can be seen, the maximum solid content is 11% WIS (due to inhibitor concentration in non-detoxified slurries).

*Table 7: Experimental parameters of SSF performed on pretreated biomass using* S.cerevisiae

| **Raw material** | **Pre-treatment** | **Amount of solids** | **Mode of operation** | **Time** | **Cellulase loading** | **β-gluc. loading** | **Ref.** |
|---|---|---|---|---|---|---|---|
| Barley straw | Steam + $H_2SO_4$ | 7.5% WIS | Batch | 120 h | 20 FPU/g[1] | 5 IU/g[1] | 1 |
| Spruce | Steam +$SO_2$ | 10% WIS | Batch | 72 h | 37.5 FPU/g[1] | 36.2 IU/g[1] | 2 |
| Spruce | Steam +$SO_2$ | 6–10% WIS | Fed-batch | 72 h | 37.5 FPU/g[1] | 36.2 IU/g[1] | 2 |
| Corn cob | Dilute $H_2SO_4$ | 7.5% w/v cell. | Shake flask | 196 h | 26 FPU/g[2] | 8:1 [3] | 3 |
| Corn stover | Dilute $H_2SO_4$ | 7.5% w/v cell. | Shake flask | 196 h | 26 FPU/g[2] | 8:1 [3] | 3 |
| Wheat straw | Dilute $H_2SO_4$ | 7.5% w/v cell. | Shake flask | 196 h | 26 FPU/g[2] | 8:1 [3] | 3 |
| Spruce | Steam +$SO_2$ | 10% WIS | Simulation | 72 h | 15 FPU/g[2] | n.a. | 4 |
| Corn stover | Steam +$SO_2$ | 10.6% WIS | Simulation | 72 h | 15 FPU/g[2] | n.a. | 4 |

*[1] (g cellulose). [2] (g WIS). [3] IU/FPU. FPU: filter paper units, IU: International unit. Typical additional experimental parameters: Temperature=35 °C to 37 °C, pH=5 , intial yest concentration=2-5 g/l. Results of the experiments are shown in Table 9. References: 1: [Linde* et al. *, 2007], 2: [Rudolf* et al. *, 2005], 3: [Wyman* et al. *, 1992], 4: [Sassner* et al. *, 2008]*

Different modes of operation have been applied, but no continuous operation has been tested. Fermentation time ranges from 72 to 196 h. To improve hydrolysis yield and rates, cellulase enzymes are usually supplemented with β-glucosidase (see section 2.3.3). The corresponding experimental results are listed in Table 9.

*Table 8: Experimental parameters of SSCF performed on pretreated biomass*

| Raw material | Pre-treatment | Amount of solids | Mode of operation | Cellulase loading | β-gluc. loading | Micro-organism | Ref. |
|---|---|---|---|---|---|---|---|
| Wheat straw | Steam + H2SO4 | 7% WIS | Batch | 21 FPU/g[1] | 25.5 IU/g[1] | *S. cerevisiae TMB3400* | 1 |
| Wheat straw | Steam + H2SO4 | 7% WIS | Fed-batch | 21 FPU/g[1] | 25.5 IU/g[1] | | 1 |
| Wheat straw | Steam + H2SO4 | 9% WIS | Batch | 21 FPU/g[1] | 25.5 IU/g[1] | | 1 |
| Wheat straw | Steam + H2SO4 | 9% WIS | Fed-batch | 21 FPU/g[1] | 25.5 IU/g[1] | | 1 |
| Corn stover | Steam + SO2 | 10% WIS | Batch | 15 FPU/g[2] | 25.5 IU/g[2] | | 2 |
| Corn stover | Steam + SO2 | 11% WIS | Fed-batch | 15 FPU/g[2] | 25.5 IU/g[2] | | 2 |
| Wheat straw | Steam + H2SO4 | 11% WIS | Fed-batch[3] | 36 FPU/g[1] | 78 IU/g[1] | | 3 |
| Corn stover | Dilute H2SO4 | 20% TS | Simulation | 12 FPU/g[1] | n.a. | *Z. mobilis* | 4 |

*Typical experimental parameters: Time=72 h to 96 h, Temperature=35 °C to 37 °C, pH=5, initial yeast concentration=2-5 g/l. [1] (g cellulose). [2] (g WIS). [3] Both substrate and enzymes were fed. FPU: filter paper units, IU: International unit. Results are shown in Table 10. References: 1: [Olofsson* et al. *, 2008a], 2: [Öhgren* et al. *, 2006], 3: [Olofsson* et al. *, 2010], 4: [Aden* et al. *, 2002]*

In Table 8 experimental parameters for SSCF carried out on pretreated wheat straw and corn stover are listed together with one data-set used in process simulation. Again, steam pretreatment with addition of $H_2SO_4$ or $SO_2$ (=dilute acid hydrolysis) was used for pretreatment and the maximum solid content in SSCF is 11% WIS. In all experiments the recombinant xylose fermenting strain *S. cerevisiae TMB3400* was used as microorganism. The simulation data shown represents the design case from NREL [Aden *et al.* , 2002]. Here a recombinant xylose fermenting *Z. mobilis* strain is utilized. In contrast to *S. cerevisiae Z. mobilis* requires a detoxification step. Moreover one should bear in mind that the operation and performance parameters given for *Z. mobilis* apply for the design case and have not yet to be proven in lab- and commercial scale.

*Table 9: Experimental results of SSF performed on pretreated biomass with* S.cerevisiae

| Raw material | Pretreatment | Hydrolysis yield | Fermentation yield | Ethanol concentration | Experiment/. Simulation | Ref. |
|---|---|---|---|---|---|---|
| Barley straw | Steam + $H_2SO_4$ | 87 %[1] | 80 %[3] | 22.4 g/l | Experiment | 1 |
| Spruce | Steam + $SO_2$ | 91 %[1] | 84 %[3] | 44.5 g/l | Experiment | 2 |
| Spruce | Steam + $SO_2$ | 91 %[1] | 84 %[3] | 44.5 g/l | Experiment | 2 |
| Corn cob | Dilute $H_2SO_4$ | 97 %[1] | 89 %[3] | 39.1 g/l | Experiment | 3 |
| Corn stover | Dilute $H_2SO_4$ | 95 %[1] | 87 %[3] | 39.1 g/l | Experiment | 3 |
| Wheat straw | Dilute $H_2SO_4$ | 93 %[1] | 86 %[3] | 38.3 g/l | Experiment | 3 |
| Spruce | Steam + $SO_2$ | ca. 90 %[2] | ca. 90 %[2, 4] | n.a. | Simulation | 4 |
| Corn stover | Steam + $SO_2$ | ca. 90 %[2] | ca. 90 %[2, 4] | n.a. | Simulation | 4 |

*[1] Hydrolysis yield was not dertermined experimentally but calculated assuming 92 % glucose to ethanol conversion. [2] No exact values are available. [3] Based on all C6 carbohydrates (in mono-, oligo- and polymeric form) in the raw material. [4] Based on C6 monomers after hydrolysis. References: 1: [Linde* et al. *, 2007]. 2: [Rudolf* et al. *, 2005], 3: [Wyman* et al. *, 1992]. 4: [Sassner* et al. *, 2008]*

In Table 9 results for the SSF experiments (and simulations) described in Table 7 are summarized. Results are shown for various types of pretreated, non-detoxified biomass. As can be seen, hydrolysis and fermentation yields around 90% (see reactions (2) and (6)) can be achieved when herbaceous biomass (straw or corn stover) or softwood (spruce) is used as substrate. Based on all C6 carbohydrates in the substrate (mono-, oligo- and polymers), this corresponds to an ethanol yield above 80%. A final ethanol concentration around 40 g/l (or ca. 4 w/w%) can be achieved. This is significantly lower than the ethanol concentrations that are reached in conventional ethanol fermentation. For the latter concentrations above 10 w/w% are possible [Jacques *et al.* , 2003]. This difference in the ethanol concentration has serious implications on the energy consumption in distillation, as will be discussed in section 2.3.8.1.

*Table 10: Experimental results of SSCF performed on pretreated biomass*

| Raw material | Pretreatment | Hydrolysis yield | C5 and C6 conversion | | Ethanol yield[1] | Ethanol concentration | Experiment/ Simulation | Ref. |
|---|---|---|---|---|---|---|---|---|
| Wheat straw | Steam + H2SO4 | n.d. | n.d. | n.d. | 75 % | 32.9 g/l | Experiment | 1 |
| Wheat straw | Steam + H2SO4 | n.d. | n.d. | n.d. | 78 % | 34.7 g/l | Experiment | 1 |
| Wheat straw | Steam + H2SO4 | n.d. | n.d. | n.d. | 59 % | 33.2 g/l | Experiment | 1 |
| Wheat straw | Steam + H2SO4 | n.d. | n.d. | n.d. | 71 % | 38.1 g/l | Experiment | 1 |
| Corn stover | Steam + SO2 | n.d. | n.d. | n.d. | 54 % | 30.3 g/l | Experiment | 2 |
| Corn stover | Steam + SO2 | n.d. | n.d. | n.d. | 59 % | 36.8 g/l | Experiment | 2 |
| Wheat straw | Steam + H2SO4 | n.d. | 50 % | n.d. | 68 % | 38 g/l | Experiment | 3 |
| Corn stover | Dilute H2SO4 | 90 % | 85 % | 95 % | 82 % | 52.6 g/l | Simulation | 4 |

[1] *Based on Xylan and Glucan in the slurry. References: 1 [Olofsson* et al. *, 2008a], 2[Öhgren* et al. *, 2006], 3 [Olofsson* et al.*, 2010], 4 [Aden* et al.*, 2002]. n.d. not determined*

Table 10 lists results for SSCF experiments together with the values for the NREL design case. The corresponding experimental parameters can be found in Table 8. Because C5 fermentation is not a top priority for woody biomass (spruce in particular) SSCF has only been performed for wheat straw and corn stover. The yields for hydrolysis and fermentation (see reactions (2), (6) and (7)) are usually not determined in SSCF experiments[31]. The key-parameter used to describe the performance of SSCF is the ethanol yield based on all carbohydrates in the substrate (C5 and C6, mono-, oligo- and polymers). As can be seen, the ethanol yields obtained in SSCF experiments are lower than those obtained in SSF (see Table 9). The lower yields are particularly a problem when SSCF is performed at a high WIS content (Reference 2), but could be avoided to some extent by using a feeding strategy for both substrate and enzymes (Reference 3). However, in comparison to SSF, SSCF still does not give the desired results and further improvements of microbes and enzymes are required. When comparing the NREL design case (Reference

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[31] *The analytical effort to complete the mass balance is significant.*

4) with experimental values, it becomes clear, that the parameters used for simulation are quite optimistic. However, one should keep in mind, that a detoxification step is considered in the NREL design case, whereas all experiments in Table 10 were performed with non-detoxified slurries.

To sum up: SSF of non-detoxified pretreated biomass with *S. cerevisiae* shows already good results and can be considered a mature technology. C6 sugars can be converted with yields similar and similar residence time as in conventional ethanol fermentation, however enzymatic conversion of cellulose should still be improved. In contrast to fermentation of C6 sugar, in SSCF (the co-fermentation of C5 and C6 sugars) the desired results have not been achieved yet. Yield improvements of SSCF, especially at high WIS content, could significantly enhance the feasibility of the technology. Data that was applied in flowsheet simulations can be found in Appendix B.

#### 2.3.4.3 Subsequent processing steps:

From SSF or SSCF an alcoholic mash (or beer) containing various soluble and insoluble solids is obtained. Cellulase enzymes act catalytically, which means that in principle they are not consumed in hydrolysis. However, separation from the beer is challenging because separation technology is costly and cellulase enzymes bind to lignin [Lynd *et al.* , 2002]. Consequently, in a SSF setup enzymes are usually not recycled but treated as part of the stillage. Product recovery and purification and stillage treatment will be discussed later in sections 2.3.8and 2.3.9.

### *2.3.5 ENZYME PRODUCTION*

In addition to the pretreated biomass and water, the fermenting microorganisms and **cellulase enzymes** are the most important components in SSF. As mentioned above, recycling of yeast and enzymes is difficult in an SSF setup and thus these biocatalysts usually have to be supplied freshly in the quantities needed.

In lignocellulosic ethanol production enzyme supply is of particular interest, because compared to starch based materials[32] much higher amounts of enzymes are needed to hydrolyze the same amount of substrate [Merino & Cherry, 2007]. This higher enzyme requirement is based on the recalcitrant nature of lignocellulosic substrates, as discussed in section 2.2. Specific production costs of cellulase enzymes (per unit of enzyme) do not differ significantly from those of amylases [Merino & Cherry, 2007]. As a result the share of enzyme costs on total ethanol production costs has been very high and a major obstacle to commercializing lignocellusic ethanol [Sims *et al.* , 2008]. However, due to intense R&D

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[32] *In conventional ethanol production amylase enzymes are utilized to hydrolyze starch to monomeric sugars.*

efforts[33] the price of cellulase enzymes recently has dropped significantly [nre, 2007], (see Fig. 2-10).

Certainly, a further reduction of enzyme costs is necessary for lignocellulosic ethanol to succeed. In principle this cost reduction can be achieved through i) more efficient enzyme production (higher yields and productivities), through ii) higher enzyme quality (higher specific enzyme activity, optimization for the particular substrate) and potentially through iii) producing the enzymes at the location of ethanol production (on-site) as will be briefly discussed in the following section.

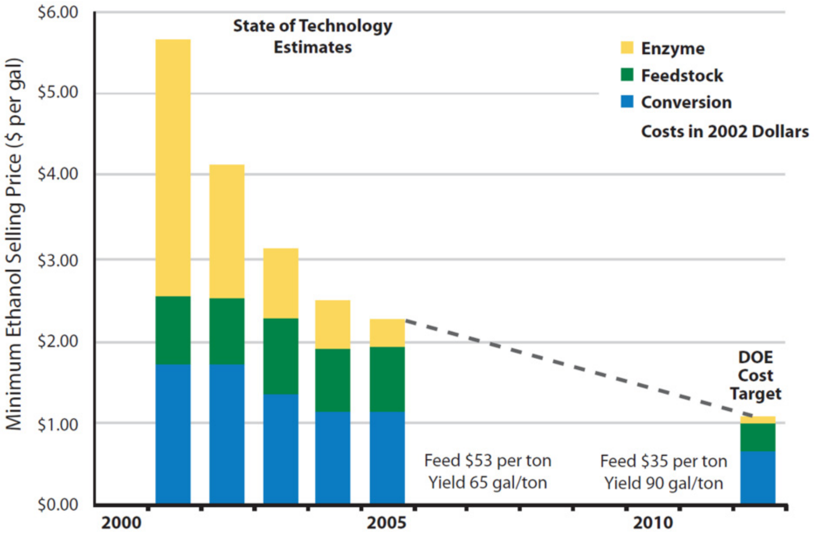

*Fig. 2-10: Development of lignocellulosic ethanol cost and the enzymes contributionenzyme. Source: [nre, 2007]*

### 2.3.5.1 Technology

In nature numerous microorganisms (bacteria and fungi) exist that produce cellulolytic enzymes [Lynd *et al.* , 2002, Merino & Cherry, 2007] however, all commercial cellulase is produced from the filamentous fungus *Trichoderma reesei* [Merino & Cherry, 2007]. The dominance of *T. reesei* in commercial cellulase production is a result of the following positive characteristics [Lynd *et al.* , 2002, Merino & Cherry, 2007]: i) *T. reesei* produces a complex mixture of enzymes that synergistically hydrolyze cellulose. ii) Over the years various optimized mutants of *T. reesei* have been developed. These mutants exhibit both high productivity and enzyme production yields. iii) *T. reesei* enzymes show a high catalytic activity. iv) Unlike most bacterial cellulase *T. reesei* cellulase is secreted into the

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[33] *Most notably in the cooperation between the US Departement of Energy (DoE) and the leading enzyme companies [Merino & Cherry, 2007].*

growth medium and not physically attached to the microorganism (extracellular enzymes). For extracellular enzymes recovery is easier and can take place without cost and energy intensive cell disintegration technologies [Chaplin & Bucke, 1990].

Industrial production of cellulase (or other enzymes) is schematically shown in Fig. 2-11. As indicated, the actual production of enzymes takes place in submerged fed batch or continuous fermentation under highly aerobic conditions (aerobic metabolism) [Tolan & Foody, 1999]. Various soluble[34] or insoluble[35] substrates induce cellulase expression in *T. reesei* mutants [Esterbauer *et al.* , 1991] and can thus be used as carbon source (food). In contrast to yeast *T. reesei* not only converts monomeric C6 sugars but also C5 sugars and the respective polysaccharides (cellulose and hemicellulose) contained in lignocellulosic biomass. In addition to air and the carbon source, nutrients have to be supplied in the enzyme production process. After fermentation the extracellular enzymes are recovered from the fermentation broth via mechanical methods [Chaplin & Bucke, 1990]. Thereafter concentration, purification and modification take place. For shipment the durability is improved through drying or addition of preservatives. Eventually the enzymes can be delivered to the ethanol production facility. All of these processing steps consume energy, add costs to the end product (enzyme) and potentially cause losses.

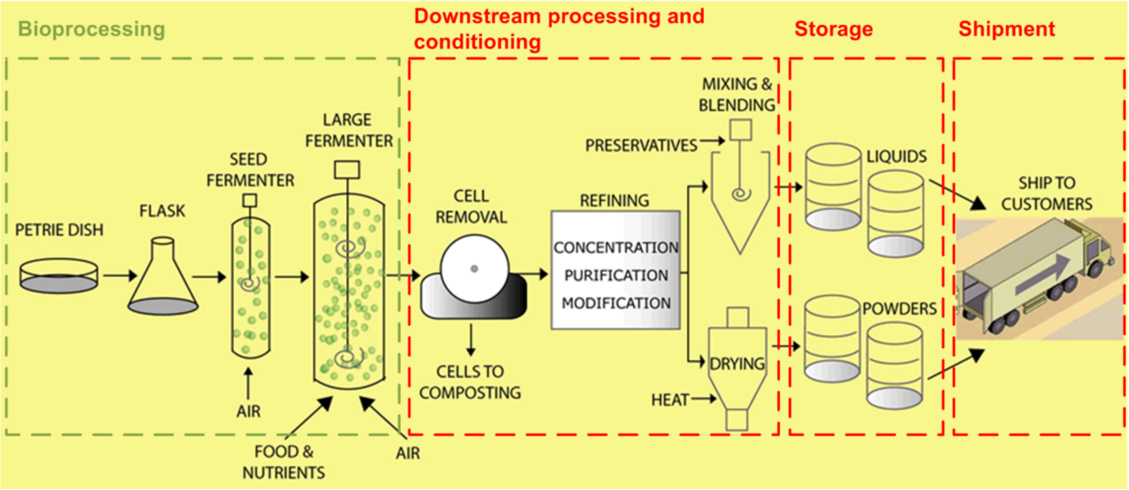

*Fig. 2-11: Industrial enzyme production. When enzymes are produced on-site, downstream processing, conditioning, storage and shipment (red) can be omitted. Adapted from: [iog, 2012]*

Presently cellulase enzymes are provided from a few large enzyme companies (Novozymes, Genencor,…) which produce in centralized facilities according to the scheme shown in Fig. 2-11. However, when enzymes would be produced at the location of

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[34] *Lactose, cellobiose or milk whey.*

[35] *Cotton, Avicel, Solka Floc or pretreated biomass.*

lignocellulosic ethanol production (on-site) the process steps downstream processing, conditioning, storage and shipment can be reduced or omitted altogether. The latter applies, when the whole fermentation broth from enzyme production is added to SSF. This strategy without any downstream processing was proposed by recent studies because no negative effects on SSF yield were observed [Kovács *et al.* , 2009, Merino & Cherry, 2007]. However, it must be noted that on-site production of cellulase enzymes also entails some disadvantages which are listed together with advantages of on-site production in Table 11. In spite of some pros for a centralized production, independent researchers [Galbe & Zacchi, 2002], [Kubicek, 2009][36] and also some enzyme producers [kot, 2008, Merino & Cherry, 2007, Tolan, 2002] believe that on-site production is the superior strategy and essential for cost effective lignocellulosic ethanol production.

As a result, throughout this work production of cellulase enzymes will take place on-site. The slurry obtained from pretreatment (see section 2.3.2) shall serve as sole carbon source.

*Table 11: Advantages and disadvantages of on-site enzyme production*

| Advantages On-site | Disadvantages On-site |
|---|---|
| No downstream processing necessary | Higher investment for ethanol production plant |
| No conditioning necessary | Less substrate for Ethanol |
| No storage and shipment necessary | No economy of scale |
| Common infrastructure | Continous improvement of production more difficult |
| Reduced cost feedstock | Plant not specialized on enzyme production |
| Tailor-made enzyme for substrate | |

### 2.3.5.2 Process Parameters

The most important process parameters for cellulase production with *T. reesei* are summarized in Table 12. Compared to SSF, much less data on enzyme production is available, because cellulase enzymes are usually bought from the suppliers who do not share their production know-how. Published data on cellulase production is often not complete[37] and thus deriving a mass balance requires combining information from different sources. As can be seen in Table 12, in 120 h various substrates yield approximately 0.3 g of enzyme per g of consumed substrate (carbohydrate). More than 90% of substrate consumption and a specific activity of ca. 600 FPU/g enzyme can be obtained.

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[36] *Personal communication with C.P. Kubicek (TU Wien) on 10.10.2009.*

[37] *Either the mass balance cannot be derived because yield is given in terms of activity or the specific activity of the enzyme was not determined.*

*Table 12: Experimental and performance parameters of cellulase enzyme production*

| **Substrate** | **Tempe-rature** | **Residence Time** | **Enzyme Yield $Y_{E/S}$[1]** | **Substrate consumption** | **Specific Activity** | **Type of reference** | **Ref.** |
|---|---|---|---|---|---|---|---|
| various substrates | - | - | 0.33 g/g | - | - | Review | 1 |
| pretreated willow | 30 °C | 120 h | - | 90% | - | Experiment | 2 |
| cellulose | 28 °C | 120 h | 0.302 g/g | 123%[2] | - | Experiment | 3 |
| pretreated spruce | 30 °C | 92 h | - | - | - | Experiment | 4 |
| various substrates | - | - | 0.27 g/g | - | 640 FPU/g[3] | Review | 5 |
| various substrates | - | - | ≥0.3 g/g | - | ≥600 FPU/g[3] | Interview | 6 |

*[1] g Enzyme produced per g Carbohydrate consumed, [2] Carbon mass balance exceeds 100% due to error in gas ($CO_2$) measurement system. [3] FPU per g of enzyme. References: 1: [Lynd* et al. *, 2002], 2: [Reczey* et al. *, 1996], 3: [Sáez* et al. *, 2002], 4: [Szengyel* et al. *, 2000], 5: [Esterbauer* et al. *, 1991], 6: Personal communication with C.P. Kubicek (TU Wien) on 10.10.2009.*

In addition to enzyme production according to equation (10), substrate is also consumed for metabolic energy supply through respiration (equation (11)) and formation of cell mass (equation (12)). The respective conversions of equations (11) and (12) are not determined in typical enzyme production studies but only during a dedicated mass balance experiment, like the one performed by [Sáez *et al.*, 2002]. The results of such an experiment are summarized in Table 13. As can be seen, 30 to 40% of carbon is converted to cellulase enzyme[38], whereas only 10 to 15% of carbon is converted to cell mass. The remaining carbohydrate (ca. 50%) is used for energy supply.

$$C_6H_{12}O_6 + rH + sO + tN \rightarrow 6CH_uO_vN_w$$

*(10) Production of cellulase enzymes ($CH_uO_vN_w$) from a carbohydrate*

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

*(11) Aerobic consumption of a carbohydrate (respiration)*

$$C_6H_{12}O_6 + dH + eO + fN \rightarrow 6CH_xO_yN_z$$

*(12) Formation of cell mass ($CH_xO_yN_z$) from a carbohydrate*

In addition to carbon, the elements hydrogen, oxygen and nitrogen have to be supplied via aeration and addition of nutrients. No literature could be found regarding the heat of reaction of enzyme production; however, according to a personal communication it is significantly smaller than the heat released during aerobic yeast propagation [Kubicek, 2009][39]. In simulations a value of 200 kJ/mol carbohydrate consumed will be assumed.

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*[38] This value corresponds well to the data in Table 12. Considering typical compositions of carbohydrates, cell mass and cellulase a yield of 0.3 g of enzyme per g of carbohydrate (see Table 12) corresponds to 35% of carbon converted to cellulase.*

*[39] Personal communication with C.P. Kubicek (TU Wien) on 10.10.2009.*

*Table 13: Carbon conversion in cellulase production*

| C to $CO_2$ Equation (11) | C to Cell mass Equation (12) | C to soluble Protein Equation (10) | Total Carbon recovery | Reference |
|---|---|---|---|---|
| 79% | 15% | 29% | 123%[1] | 1 |
| 50% | 10% | 40% | 100% | 2 |

*[1] Carbon recovery exceeds 100% due to error in gas ($CO_2$) measurement system. References: 1: [Sáez* et al. *, 2002], 2: Personal communication with C.P. Kubicek on October 10th 2009*

To sum up: enzyme production on part of the pretreated biomass is a promising strategy to reduce production costs and will be considered in this work. Compared to SSF, only limited data is available for enzyme production, especially when lignocellulsic substrates are used. Data that was applied in flowsheet simulations can be found in Appendix B.

## *2.3.6 YEAST PRODUCTION*

In conventional ethanol production from sugar or starchy crops the fermenting yeast (*S. cerevisiae*) is produced at the production site for economic reasons [Jacques *et al.* , 2003]. In ethanol production from lignocellulosic feedstock on-site propagation of yeast is considered necessary for the same reason [Aden *et al.* , 2002, Sassner *et al.* , 2008]. Because recycling of the yeast is not possible when SSF technology is used[40], new yeast has to be produced in the amounts required. As a carbon source for yeast propagation purchased glucose or molasses can serve, however, pretreated biomass[41] **enriched** with glucose or molasses is advantageous for two reasons. First, when part of the pretreated biomass is used for yeast propagation less of the substrate has to be purchased, and second, yeast cultivated on pretreated biomass is better adapted to the toxic conditions in SSF [Rudolf *et al.* , 2005]. Enrichment with monomeric C6 sugars is necessary due to the low sugar concentration in the slurry or liquid obtained from pretreatment.

### 2.3.6.1 Process parameters

In contrast to ethanol fermentation, yeast propagation is performed using an aerobic metabolism (respiration), as described by equation (11). This metabolism is desired, since both yield and productivity are much higher than in anaerobic metabolism. To prevent the "Crabtree effect"[42] intense aeration and slow addition of substrate (fed batch cultivation) is necessary [Dellweg, 1987]. Aerobic yeast production is a highly exothermic bioprocess during which approximately 1000 kJ of heat are released per mol of glucose consumed [Einsele *et al.* , 1985]. To maintain the operating temperature at the desired level cooling (internal or external) is thus mandatory. Yeast cell mass is formed according to equation

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*[40] A separation from the other insoluble solids (mainly lignin) after fermentation is not possible.*

*[41] The whole slurry or only the separated liquid fraction (pretreatment liquid).*

*[42] The Crabtree describes the effect that at high sugar concentrations anaerobic metabolism (ethanol fermentation) takes place despite aeration [Dellweg, 1987].*

(12)[43]. In Table 14 process data for yeast propagation on molasses and on enriched pretreatment liquid is summarized.

*Table 14: Process data for yeast propagation*

| Substrate | Temperature | Residence Time | Biomass Yield $Y_{X/S}$[2] | Final cell mass conc. | Mode of operation | Ref. |
|---|---|---|---|---|---|---|
| Molasses | 30 °C | 15 h | 0.54 g/g | 148 g/l | Aerobic fed-batch | 1 |
| Enriched PL[1] | 30 °C | - | 0.5 g/g | 40 g/l | | 2 |
| Enriched PL[1] | 30 °C | 16 h | 0.48 g/g | 17 g/l | | 3 |

*[1]Pretreatment liquid (PL) enriched with molasses [2]g yeast per g sugar consumed. References: 1: [Dellweg, 1987], 2: [Sassner* et al. *, 2008], 3: [Rudolf* et al. *, 2005]*

As can be seen, temperature, residence time and product yield are quite similar for pure molasses and enriched pretreatment liquid. Per g of sugar consumed ca. 0.5 g of yeast biomass are obtained. This mass yield corresponds to ca. 60% of carbon converted to yeast biomass. The remaining 40% are utilized for energy supply according to equation (11). When enriched pretreatment liquid is used as a substrate the final cell mass concentration is much lower than with molasses. However, for an SSF process the rather low concentration of yeast obtained is sufficient, because before SSF the pretreatment slurry has to be diluted anyway. Data that was used in flowsheet calculations is listed in Appendix B.

### *2.3.7 NUTRIENTS FOR BIOREACTORS*

In any biotechnological process, a carbon source is converted to carbonaceous products in an aqueous environment. In the bioreactors considered in this work, sugars are converted to the main metabolites ethanol, $CO_2$ and water (which exclusively consist of C, H and O) as well as to microbial biomass and cellulase enzymes. In contrast to the main metabolites, microbial biomass and enzymes also contain N, P, S, minerals and trace elements. These elements can not be obtained from the carbon source and have to be added as **nutrients.** For the economics of biotechnological processes is of great importance that the costs of nutrients are low and that the nutrients optimally support the formation of the desired products.

**Corn steep liquor (CSL)** is a cheap and effective option for providing the necessary nutrients. CSL is obtained as a by-product of starch production and is characterized by a high content of protein (nitrogen). Furthermore, CSL contains essential minerals and vitamins [cra, 2006]. For bioethanol fermentation as well as for cellulase production CSL is highly suitable [Aden *et al.* , 2002, Humbird *et al.* , 2011]. The composition of CSL is shown in Table 15.

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[43] *Equation (12) shows the generic formation of cell mass ($CH_xO_yN_z$) from a carbohydrate. The composition of* S.cerevisiae *and* T. reesei *is slightly different, thus the indices x, y and z differ.*

Since CSL contains only small amounts of phosphorus, it can be supplemented with **diammoniumphosphate** (**DAP**, $(NH_4)_2HPO_4$). DAP is a suitable source for both nitrogen and phosphorus and provides the nutrients in a form that supports microbial uptake and conversion (by both by *S. cerevisiae* and *T. reesei*). Per gram, DAP contains approximately 0.21 g N and 0.23 g P.

If Phosphorus needs to be added independently from nitrogen, DAP is not suitable. This may be the case in anaerobic digestion or during aerobic wastewater treatement. In these cases, **phosphoric acid (H3PO4)** can be used. Per gram, phosphoric acid contains some 0.32 g of P.

As outlined in section 2.3.4, convetional yeast can only utilize C6 sugars. However, pretreated biomass contains only very small amounts of monomeric C6 sugars. Therefore, enrichment of pretreated biomass with an additional carbon source is necessary. A cheap and suitable substrate for this purpose is **beet molasses**. The composition of molasses is shown in Table 15.

The respective amount of nutrients that must be added in the individual bioreactors, are obtained by calculating the demand based on elementary balances (see Appendix A).

*Table 15: Composition of the nutrients corn steep liquor and beet molasses*

| | **Corn steep liquor (CSL)** | **Beet molasses** |
|---|---|---|
| **Composition [w/w%]** | | |
| Solids | 50% | 80% |
| Sugar (Sucrose) | n.a. | 40-50% |
| Nitrogen | 4% | 1.5% |
| Proteins | 23% | n.a. |
| Water | 50% | 20% |
| Ash | 8% | 10.3 |

*Data Sources for Corn steep liquor: [cra, 2006]; Beet molasses: [Dellweg, 1987]*

### *2.3.8 PRODUCT RECOVERY AND PURIFICATION*

From SSF an alcoholic mash[44] with ca. 4% ethanol is obtained. The actual ethanol concentration depends on the solids content in hydrolysis, the SSF yield and the sugar content[45] in the raw material. In addition to water (by far the largest fraction) and ethanol, a variety of other liquid, solid (soluble and insoluble) and gaseous compounds make up the alcoholic mash (see Table 16).

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[44] *Alternatively the term **beer** is used.*

[45] *Both mono- and polymonosaccharides.*

*Table 16: Components in the mash obtained from SSF of pretreated lignocellulosic biomass*

| Insoluble solids | Soluble solids | Liquids | Gases |
|---|---|---|---|
| Lignin | Unconverted sugars[2] | Water | Dissolved $CO_2$ |
| Unconverted Cellulose | Enzymes | Ethanol | |
| Unconverted Hemicellulose | Plant extractives | Acetic Acid | |
| Mircoorganisms[1] | Soluble plant protein | Glycerol | |
| Insoluble ash | Soluble ash | Furfural | |
| | Soluble lignin | HMF | |
| | Other soubles[3] | Other liquids | |

*[1]Yeast and T. reesei [2]Mono- and oligomers, mainly C5 [3]organic or inorganic (sulfur and ammonia from pretreatment)*

### 2.3.8.1 Distillation

To recover ethanol from this highly-complex mixture distillation[46] is the most suitable technology [Aden *et al.* , 2002, Sassner *et al.* , 2008, Larsen *et al.* , 2008]. After $CO_2$, ethanol has the highest vapor pressure of the listed compounds and can thus be recovered rather easily with distillation. However, the high amount of solids renders the distillation of lignocellulosic mashes technically challenging. Insoluble solids can block the columns or cause fouling and thus special equipment, is necessary for lignocellulosic mashes (see Fig. 2-12 a). Moreover, the ethanol content in lignocellulosic mashes is much lower (ca. 4%) than in mashes obtained from conventional ethanol production (8-10%). This low ethanol concentration leads to increased investment cost for distillation. For the same amount of product approximately the double amount of feed enters the distillation section which has to be sized correspondingly larger. As shown in Fig. 2-12 b), a low ethanol content in the feed also increases the specific energy demand for distillation. The importance of a high WIS content in SSF (which is a prerequisite for a high ethanol concentration, see section 2.3.4) thus becomes clear.

A **multi-column setup** is state of the art in both conventional [W.M. Ingledew & Kluhsies, 2009] and lignocellulosic ethanol production [Aden *et al.* , 2002, Sassner *et al.* , 2008, Larsen *et al.* , 2008]. In a stripper column ethanol is pre-concentrated and separated from solids, which are recovered at the bottom of the column. The pre-concentrated ethanol-water mixture is obtained at the top or a side draw of the stripper column and fed to a rectification column in whose head condenser a nearly azeotropic mixture of ethanol and water (95.6 w/w%, [W.M. Ingledew & Kluhsies, 2009]) is gained. Liquids that are less volatile than ethanol are removed at the bottom of the stripper or rectification column.

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[46] *Fundamentals and theory of distillation can be found in dedicated textbooks such as [Stichlmair & Fair, 1998].*

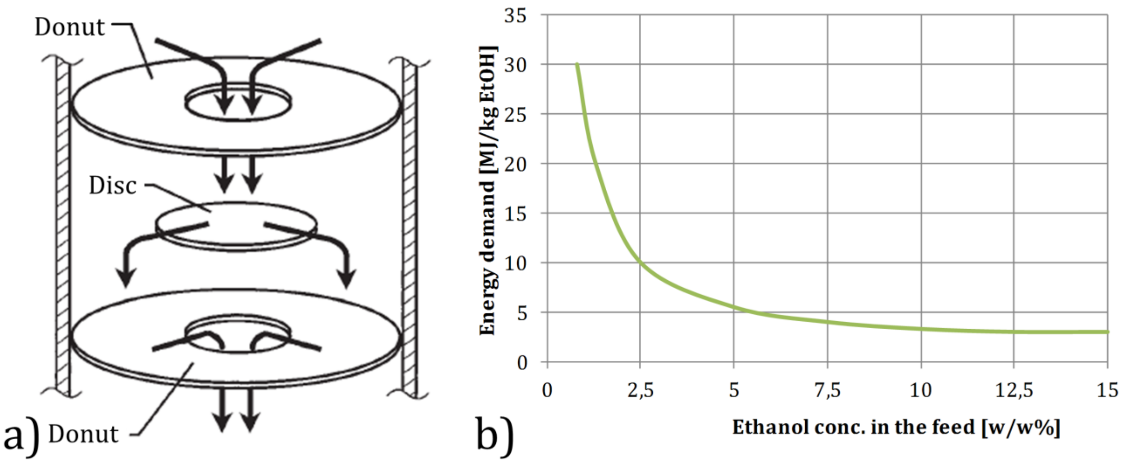

*Fig. 2-12: a) Disc and Donut trays for the distillation of high-fouling feed streams. Source: [W.M. Ingledew & Kluhsies, 2009]. b) Specific energy demand for the distillation of low concentration feed streams. Adapted from [Zacchi & Axelsson, 1989]*

To reduce the energy demand of the distillation section the columns can be **integrated thermally** (heat integrated). The temperature difference that is necessary for heat recovery between the columns is achieved by operating the columns at different pressures [Stichlmair & Fair, 1998]. A possible distillation setup for column integration proposed by [Wingren *et al.* , 2008] consists of two parallel stripper columns (one pressurized and one operated under atmospheric conditions) and one vacuum rectifier column.

Another strategy to save energy in distillation is to thermally integrate the distillation section with other process parts that consume or provide thermal energy. Following this strategy, a distillation setup with one stripper and one rectifier column operated at similar pressure levels (1.8 and 1.6 bar) was proposed [Aden *et al.* , 2002].

Heat integration of the lignocellulosic ethanol process is dealt with in section 3.3 and ***Paper II***. Different setups for distillation and evaporation (see section 2.3.9.2) are discussed. It was found that integration with the background process is the best strategy to minimize the overall process energy demand. Flowsheeting assumptions can be found in Appendix B.

#### 2.3.8.2 Pressure swing adsorption

The maximum concentration of ethanol that can be reached with distillation of an aqueous solution is defined by the azeotropic point. However, when ethanol is used as a gasoline blend higher purity is required (maximum water content 0.3 w/w%, minimum ethanol content 98.7 w/w%[47] according to ÖNORM EN 15376) and thus other technologies have to

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[47] *Including a maximum of 2 w/w% of higher alcohols.*

be applied. The industrial standard for ethanol purification of nearly azeotropic mixtures is **pressure swing adsorption (PSA)** [Jacques *et al.* , 2003].

In PSA, small water molecules are selectively adsorbed in the pores of a zeolite bed at elevated pressure. On the other hand larger ethanol molecules cannot enter the zeolite pores and pass the bed without being adsorbed. A high purity ethanol product leaves the adsorber [48]. After a certain time of operation the bed is loaded with water and no further adsorption takes place. When this point is reached the bed has to be regenerated. Thereto the pressure is reduced and the bed is purged with ethanol. After completed regeneration another cycle can start.

In industrial practice continuous operation of the PSA is required and thus an industrial PSA setup consists of two beds. During adsorption in bed 1, bed 2 is being regenerated using part of the purified ethanol product obtained from bed 1 and vice versa. The purging fluid obtained from regeneration has to be returned to the rectifier column [Jacques *et al.* , 2003].

Most PSA setups operate in the gas phase with slightly superheated vapors [Jacques *et al.* , 2003]. The ethanol product from distillation is typically obtained in vaporous form and so the amount of direct thermal energy needed for PSA is relatively small compared to distillation[49]. In Table 17 the most relevant operating parameters for PSA are summarized.

*Table 17: Operating parameters in pressure swing adsorption (PSA)*

| **Adsorption pressure** | **Adsorption temperature** | **Purge ratio** | **Heat requirement[2]** | **Electricity requirement[3]** | **Ref.** |
|---|---|---|---|---|---|
| 1.7 atm | 116 °C | - | - | - | 1 |
| 3.8 atm | 166 °C | - | - | - | 2 |
| - | - | 15-40%[1] | 70-105 kJ/kg ethanol | 24-37 kJ/kg ethanol | 3 |

*[1]% of ethanol product needed for regeneration [2]Heat for superheating the vapors [3]Electrical energy for pumps, compression, etc. Per kg of ethanol product. References: 1: [Aden* et al. *, 2002], 2: [Simo* et al. *, 2008], 3: [Jacques* et al. *, 2003]*

The high-purity ethanol product obtained from PSA is condensed and cooled. After denaturation the product is ready for shipment. Flowsheeting assumptions can be found in Appendix B.

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[48] *Down to 20 ppm water are possible. For fuel ethanol 99.5% are sufficient.*

[49] *However, one has to keep in mind that up to 40% of ethanol (see Table 17) are returned to rectifier in condensed form which increases the energy demand in distillation.*

### 2.3.9 STILLAGE TREATMENT IN LIGNOCELLULOSIC ETHANOL PRODUCTION

The term **stillage** is used for the bottom product of distillation. Apart from $CO_2$ and ethanol, lignocellulosic stillage contains all the components that are listed in Table 16. With more than 80 w/w%, water is the major component of stillage. However, as outlined in section 2.1 at least 35% of the feedstock are not converted to ethanol and end up in the stillage. As a result, a significant share of the feedstock's energy is contained in the stillage. These numbers impressively illustrate the significance of i) water recovery technologies that enable the recirculation of process water and ii) by-product recovery from the stillage (see section 2.4). Of course, low energy use and low investment costs are mandatory in meeting these tasks.

#### 2.3.9.1 Solid – liquid separation

A first step in stillage treatment is typically the mechanical separation of insoluble solids from the aqueous phase[50] [Sassner *et al.* , 2008, Aden *et al.* , 2002]. Mechanical methods are used because of their low energy requirement and a good separation of insoluble compounds (lignin, cellulose, yeast,…) from the liquid phase.

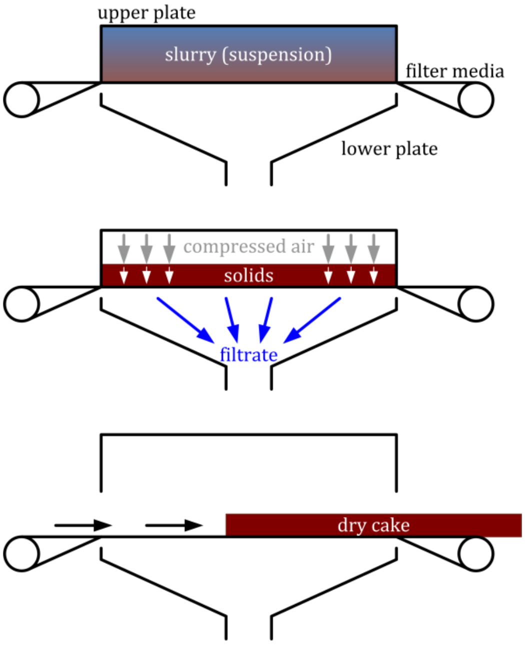

*Fig. 2-13: Operating principle of Pneumapress. Adapted from [Harris Group Inc., 2001]*

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[50] *The aqueous phase also contains other liquids and soluble solids listed in Table 16.*

For the solid – liquid separation of lignocellulosic stillages various technologies such as centrifuges, filter presses, belt filter presses, horizontal belt filters, Pneumapress pressure filters and extractors are available [Harris Group Inc., 2001]. The aforementioned technologies were tested and evaluated and the **Pneumapress pressure filter** was found to be the best solution [Harris Group Inc., 2001]. With this equipment, whose operating principle is shown in Fig. 2-13, both a high drymatter content of the cake (up to 55%) and high recovery of insoluble solids in the cake (>99.5%) can be achieved [Harris Group Inc., 2001, Aden *et al.* , 2002].

In this type of filter, pressurized air is used to force the liquids out of the cake. The spent air can be reused in other process parts [Aden *et al.* , 2002]. Another advantage of this equipment lies in the fact that in can be operated at elevated pressures and temperatures, i.e. above the atmospheric boiling temperature of water [Harris Group Inc., 2001, Nagle *et al.* , 2002]. Thus, a cooling of the hot stillage prior to the separation and a possible re-heating of the liquid (filtrate) or solids (cake) can be avoided. This reduces both the energy requirement of the process and the need for heat exchange equipment. At this point it must be mentioned that a solid – liquid separation can also take place directly after the pretreatment [Larsen *et al.* , 2008]. However, this is feasible only when i) straw is used as a substrate and ii) pentoses are not co-fermented with hexoses[51]. When this process design is chosen soluble toxic (Furfural, HMF,…) compounds are removed with the liquid and the SSF can be performed at a higher WIS [Larsen *et al.* , 2008]. Flowsheeting assumptions can be found in Appendix B.

### 2.3.9.2 Evaporation of the liquid fraction

Evaporation is a standard technology for the separation of liquids (solvents) and non-volatile compounds (solids) contained in the solvent. As the name implies, in evaporation the solvent is evaporated and condensed separately from the residual solids. In principle evaporation can be applied for the separation of suspensions[52] and single-phase liquids with dissolved solids; however within this work evaporation is only considered after a solid – liquid separation step (see section 2.3.9.1) [Aden *et al.* , 2002, Sassner *et al.* , 2008]. Apart from water the evaporated solvent also contains other volatile compounds (acetic acid, furfurals, alcohols…). In principle these volatile compounds could hinder the recirculation of process water due to their toxicity but it was experimentally determined that the condensed vapors obtained from evaporation of spruce stillage[53] could be recycled to the up-stream process without negative effects [Larsson *et al.* , 1997].

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[51] *When spruce is pretreated, many hemicellulose derived hexoses are recovered in the liquid fraction and would be lost for ethanol fermentation.*

[52] *Liquids containing insoluble solids.*

[53] *i.e. the stillage that results from steam pretreatment (section 2.3.2), SSF (section 2.3.4) and distillation (section 2.3.8.1) of spruce.*

Evaporation is thus a suitable technology to recover process water from lignocellulosic stillages. Certainly, when the process water cycle is closed, the concentration of toxic compounds will increase with each cycle. Thus only a part[54] of the condensed vapors can be recycled to the up-stream process.

In evaporation a part of the feed stream undergoes a phase change and therefore the enthalpy of vaporization has to be supplied; the energy demand of evaporation is accordingly high. In order to reduce this high energy demand of evaporation various measures exist, the most common one is **multi-stage evaporation**[55]. Here the vapors from one stage replace the hot utility in the subsequent stage. Heat only has to be supplied at the first and removed at the last stage. In order to enable the heat transfer a temperature difference between the stages is necessary (ca. 5-10 °C). Thereto the stages are operated at different pressures. When two stages are used instead of one, the energy demand is approximately halved. However, with increasing number of stages the energy reduction per additional stage becomes smaller and smaller whereas the investment costs increase. The optimal number of stages is thus a trade-off between energy and investment costs [Mersmann, 2005]. In practice three to five stages are typically used [Aden *et al.* , 2002, Sassner *et al.* , 2008]. Heat integration between the evaporation section and the other parts of the process is another strategy to reduce the overall process heat demand. More information about this topic can be found in section 3.3 and ***Paper II***. Flowsheeting assumptions can be found in Appendix B.

As mentioned above the condensed vapors can partly be recycled to the up-stream process. The concentrate (or syrup) can be concentrated up to 65% DM [Larsen *et al.* , 2012]. Options for by-product recovery from the concentrate will be discussed in section 2.4.

#### 2.3.9.3 Drying of solids

The solid fraction after the solid – liquid separation is mainly made up of lignin but also contains unconverted cellulose, hemicellulose, ash, yeast and residual soluble solids. Moreover this fraction still contains a significant amount of water (>45%, see section 2.3.9.1) that needs to be removed by means of drying. Drying is a method to remove moisture from a solid and in principle a multitude of drying methods exist. A description of these methods can be found in dedicated textbooks (e.g. [Mersmann, 2005]).

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[54] *The recycle ratio at which inhibition occurs depends on many variables and has to be determined experimentally for the specific setup.*

[55] *Other measures to reduce the energy demand in evaporation (e.g. mechanical and thermal vapor recompression techniques) exist but are not covered within this work. For further information see various textbooks (e.g. [Mersmann, 2005]).*

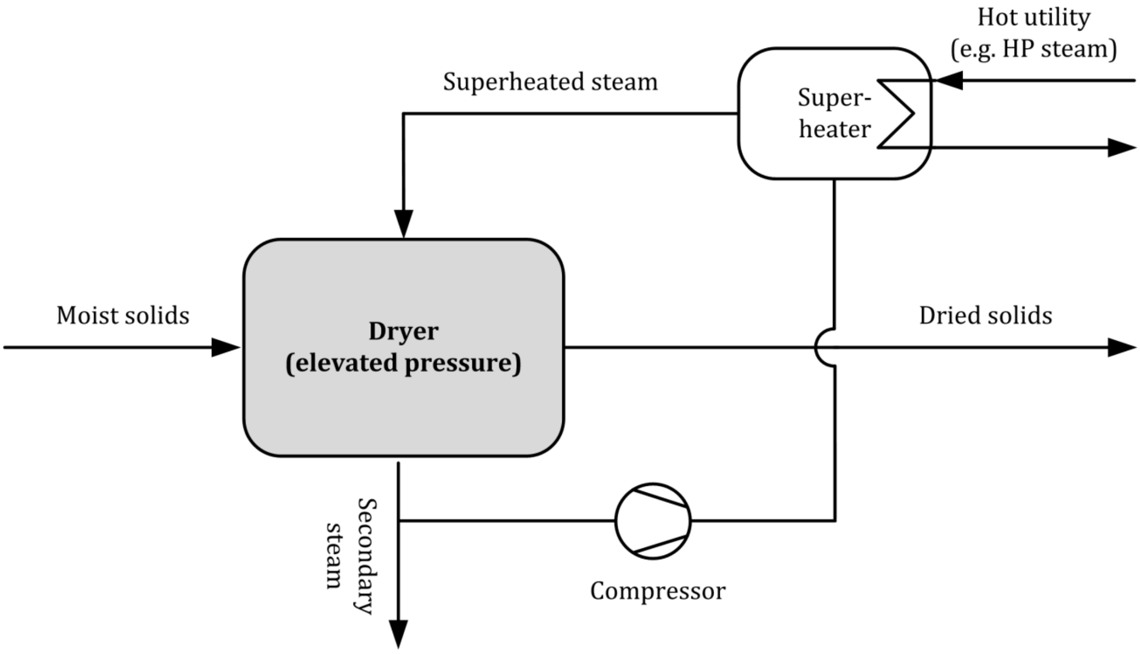

*Fig. 2-14: Operating principle of a superheated steam dryer. Adapted from [gea, 2012]*

Just as distillation and evaporation drying is an energy intensive unit operation. An energy-efficient drying technology is thus desired. For drying of the solid fraction of the lignocellulosic stillage **superheated steam drying** has been proposed [Sassner *et al.* , 2008]. The operating principle of a superheated steam dryer is shown in Fig. 2-14. As the name implies, superheated steam is used as the drying medium. In the dryer this superheated steam is brought in direct contact with the moist solids. The heat transfer between superheated steam and the solids results in i) a cool down of the superheated steam to saturation conditions and ii) the drying of solids, i.e. the evaporation of water from the solids. To separate the dried solids form and saturated secondary steam[56] a cyclone is typically used. A part of the secondary steam is recirculated, superheated (in the superheater) and reused as drying medium in the next cycle. Excess secondary steam can be used to heat other parts of the process. By generating secondary steam a major part of the energy used for drying is recovered at a lower temperature level. Reuse of this energy reduces the overall process heat demand and positively affects the net energy balance. This is the main reason why superheated steam drying is a good choice in bioenergy production processes. More information about process heat integration can be found in section 3.3 and ***Paper II***. Flowsheeting assumptions can be found in Appendix B. The valorization of the dried solids is discussed in section 2.4.

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[56] *Originating from i) superheated steam and ii) evaporated water.*

### *2.3.10 BIOGAS PRODUCTION FROM LIGNOCELLULOSIC STILLAGE*

As outlined in section 2.3.9 a rather large share of the feedstock's energy potential is recovered in the stillage. To utilize this potential, biogas can be produced via **anaerobic digestion (AD)** of the stillage. Biogas is a mixture of mainly $CH_4$ and $CO_2$ that is usually produced from energy crops, organic wastes or waste waters (see Table 1 in section 1.2). Biogas is typically converted to electricity and heat in gas engines. Alternatively to co-generation in gas engines biogas can be upgraded to natural gas quality and thereafter be fed to the gas grid or sold in gas stations. A third option for biogas utilization is the direct combustion to provide heat. This strategy is often applied in the water treatment plant of industrial facilities.

#### 2.3.10.1 Technology

Biogas (mainly $CH_4$ and $CO_2$) is formed during the anaerobic digestion of organic material ($C_nH_aO_bN_c$). In AD, a consortium of anaerobic microorganisms converts organic matter in a series of biochemical reactions (hydrolysis, acidogenesis, acetogenesis, methanogenesis) [Bischofsberger *et al.* , 2009]. The end product of this biochemical chain of reactions is biogas. In addition to the main constituents $CH_4$ and $CO_2$ biogas may additionally contain water vapor, $H_2S$, $NH_3$, siloxanes, higher hydrocarbons and other minor components [Urban *et al.* , 2009]. Moreover, microbial biomass (anaerobic sludge) is formed during anaerobic digestion. A major strength of AD is its simplicity and the fact that no energy intensive product recovery technology is necessary. Unconverted organic matter, water and sludge remain in the reactor whereas the gaseous product escapes at the top. The major weakness of AD is the speed of the reactions; the typical **hydraulic retention time (HRT)** in AD is in the order of weeks or months [Wilkie, 2008].

In principle lignocellulosic stillage is well suited for AD. Through pretreatment and enzymatic hydrolysis the material is in a condition that promotes microbial conversion. This is particularly true for straw stillage which contains a large fraction of soluble C5 sugars that are not converted by *S. cerevisiae.* But not only unconverted sugars are utilized in AD; also other components such as proteins, extractives and even compounds that are toxic for yeast can be converted to biogas in AD. On the other hand the stillage contains components that can not be converted (or only to a very limited extent) in AD (lignin, cellulose). As outlined above, in lignocellulosic ethanol production biogas production serves two purposes. First, an established by-product is recovered from the stillage and second, biogas production serves as a first step in treatment of waste waters from the process. Combined with solid-liquid separation and a subsequent aerobic treatment of waste-waters, AD can replace [Barta *et al.* , 2010] or complement [Aden *et al.* , 2002] the energy intensive evaporation of the stillage. A big advantage of AD compared to other technologies for stillage treatment is the fact that nutrients (nitrogen and minerals) remain in the anaerobic sludge and can thus be recycled to the agricultural system to replace mineral fertilizer.

Basically three process options exist for the production of biogas from lignocellulosic stillage (see Fig. 2-15). In case 1) the whole stillage including insoluble solids is fed to the biogas reactor. Compared to the other options, more organic matter is fed to the reactor which results in the highest biogas potential. However, the insoluble solids (lignin, cellulose) are more persistent than soluble solids. As a result a higher residence time and/or lower conversion compared to the other options can be expected. Moreover, only conventional stirred tank reactors can be employed for this kind of substrate [Bischofsberger *et al.* , 2009]. This option will henceforth not be considered. In case 2) persistent insoluble solids are removed (see section 2.3.9.1) prior to AD. This results in a lower biogas potential compared to case 1) however, a higher conversion and shorter residence times can be expected. Moreover, since no insoluble solids are contained in the substrate, high performance reactors used for waste water treatment can be employed [Bischofsberger *et al.* , 2009]. This options is most promising and thus within this work it will be the only option considered (see section 3.1.3). In case 3) the stillage is not used for biogas production. Instead AD is used to treat waste waters obtained from various process steps (e.g. steam explosion, drying, evaporation,…) before recycling them to the process [Aden *et al.* , 2002]. This option is not suitable to recover by-products from the stillage and will henceforth not be considered.

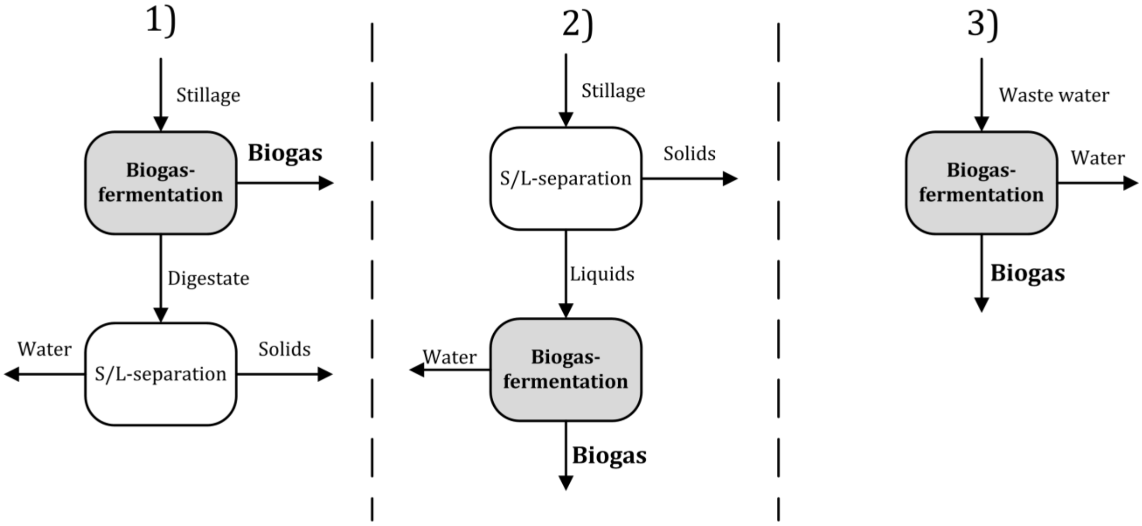

*Fig. 2-15: Options for biogas production from lignocellulosic stillage. 1) Whole stillage [Barta* et al. *, 2010], 2) Liquid fraction of stillage only [Barta* et al. *, 2010], 3) Process waste water only [Aden* et al. *, 2002]*

As outlined above, the type of reactor used for AD depends on the substrate. For solid substrates (energy crops or case 1)), **continuously stirred tank reactors (CSTR)** are used. CSTRs are simple but can only be operated with high HRT and low **organic loading rate (OLR)** [Bischofsberger *et al.* , 2009].

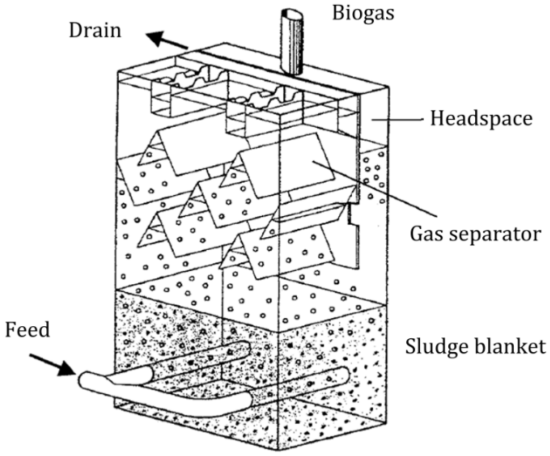

*Fig. 2-16: Upflow anaerobic sludge blanket (UASB) reactor. Adapted from [Bischofsberger* et al.*, 2009]*

As a result large fermentors with high investment costs are required. On the other hand, for waste waters (option 2) and 3)) various types of high performance reactors with biomass retention exist. The most commonly used type is the **upflow anaerobic sludge blanket reactor (UASB)** [Bischofsberger *et al.* , 2009, Wilkie *et al.* , 2000]. As can be seen in Fig. 2-16, the UASB reactor is fed from the bottom and the feed flows through a blanket of retained sludge (microbial biomass). These reactors allow for much a higher loading rate which results in much smaller reactors and lower investment costs.

### 2.3.10.2 Process parameters

To quantitatively describe the overall reaction[57] of biogas formation from organic matter the Buswell equation (13) can be used. As can be seen, during AD carbon undergoes a **disproportionation** reaction. Carbon in the substrate (oxidation state≈0[58]) is partly oxidized to carbon dioxide (+IV) and partly reduced to methane (-IV). All the chemical energy is conserved in one component of the product gas mixture (methane); carbon dioxide removal (see section 2.3.10.3) can thus yield a high quality gaseous product.

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[57] *Without considering intermediate steps.*

[58] *The oxidation state depends on the type of substrate. For carbohydrates the average value is 0.*

$$C_nH_aO_b + (n - \frac{a}{4} - \frac{b}{2})\, H_2O \rightarrow (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})\, CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})\, CH_4$$

*(13) Biogas formation according to Buswell [Buswell & Mueller, 1952]*

The most important parameter in AD is the **fractional conversion** of organic matter according to equation (13). However, in practice, the formation of biogas is usually not expressed as fractional conversion of reaction (13) but as **methane yield** per kg of organic matter. This value is known for the most common substrates and is typically given in the unit $Nm^3$ $CH_4$/kg volatile solids[59] (VS).

A third method to quantify the conversion in AD is to define the removal of **chemical oxygen demand (COD)** from the substrate. This method is often used in process modeling [Aden *et al.* , 2002, Barta *et al.* , 2010]. The COD is a parameter from water treatment technology and is used to quantify the amount of degradable organic components in water. It is defined as the amount of oxygen ($O_2$) that is necessary for complete oxidation of the organic compounds in a sample (see equation (11)).

$$C_nH_aO_bN_c + (n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c)O_2 \rightarrow nCO_2 + (\frac{a}{2} - \frac{3}{2}c)H_2O + cNH_3$$

*(14) Definition of COD [Sawyer* et al.*, 2003].*

The COD value of a sample is usually determined and expressed as concentration (g/l); Since the COD is a measure for the quantity of organic compounds it also can be used to express the mass (kg) or mass flow (kg/h) of organic matter.

$$m_{COD,feed} = m_{COD,digestate} + m_{COD,gas}$$

*(15) Conservation of the COD during AD.*

$$COD\ removal = \left(1 - \frac{m_{COD,digestate}}{m_{COD,feed}}\right) * 100\%$$

*(16) COD removal in %.*

*where $m_{COD,i}$ denotes the mass of COD in stream i*

As described previously, in AD organic matter (i.e. COD) is converted to biogas. Since the conversion of substrate takes place under anaerobic conditions, no net oxidation occurs during AD. The mass of COD ($m_{COD}$) is thus conserved during biogas formation and equation (15) applies[60] [Batstone *et al.*, 2002]. COD (or chemical energy) is merely shifted (or removed) from the substrate and transferred to methane. As can easily be checked, one kg of COD removed from the substrate yields 350 NL of $CH_4$ [Wilkie, 2008][61]. The

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[59] *Volatile solids is a measure for the amount of organic drymatter [Sawyer* et al.*, 2003].*

[60] *To verify equation (15), apply equation (14) to the left hand and right hand side of equation (13).*

[61] *According to theory. In practice deveations can be observed, see Table 18.*

removal of COD, as expressed in equation (16), is thus a measure for the substrate conversion in AD. For a substrate without nitrogen (e.g. a carbohydrate) the COD removal and the percent conversion according to Buswell (equation (13)) are identical[62].

Besides describing the conversion in AD, the COD is also used to describe the organic loading rate of the fermenter (e.g. in kg COD/m$^3$d) or can be used to derive the microbial nutrient demand in AD. For the latter typical values are $COD_{removed}$:N:P =1000:5:1 to 350:5:1 [Bischofsberger *et al.* , 2009]. Moreover, the removal of COD is suited to estimate the amount of sludge formed in AD. Typically, 0.03 – 0.15 kg sludge are formed per kg $COD_{removed}$ [Wilkie, 2008].

*Table 18: Anaerobic digestion of cellulosic stillage and molasses. All data from [Wilkie* et al.*, 2000]*

| **Substrate** | **Reactor Type** | **Influent COD [g/L]** | **HRT[3] [d]** | **COD OLR[4] [kg/m$^3$d]** | **COD removal [%]** | **$CH_4$ Yield [NL/kg COD]** |
|---|---|---|---|---|---|---|
| Cellulosic | -[1] | -[1] | -[1] | 9.48 [1] | 83.56% [1] | 300 [1] |
| Beet molasses | UASB | 10 | 0.58 | 13.8 | 55.4% | 360 |
| Cane molasses | UASB | 15.2 | 0.83 | 18.3 | 76% | 280 |
| Cane molasses | UASB | 100 | 10 | 10 | 67% | |
| Cane molasses | UASB | 109 | 6.8 | 16 | 67% | |
| Cane molasses | UASB | 68.9 | 3.2 | 21.5 | 58% | 170 |
| Cane molasses | UASB | 46 | 2 | 23.3 | 71.3% | 220 |
| Cane molasses | HUASB[2] | 103 | 0.25 | 36 | 80% | 400 |
| Cane molasses | UASB | 88 | 4.4 | 20 | 61% | 280 |

*[1] Average value of six data sets are presented, different reactor types were used. [2] HUASB…Hybrid UASB [3]HRT…Hydraulic retention time. [4] OLR…Organic loading rate*

In Table 18 experimental data for anaerobic digestion of lignocellulosic stillage and molasses are summarized. The conversion of substrate is defined by the removal of COD. In addition, the concentration of organic matter in the feed (also given as COD), the loading rate and the hydraulic retention time ared lister. As can be seen limited data is available for lignocellulosic stillage. To supplement the information, data for molasses (beet and cane) is additionally listed in Table 18. The composition of the liquid fraction of straw stillage is quite similar to that of beet or cane molasses, with the difference that C5 sugars are present instead of C6 sugars[63]. The data for molasses can thus give valuable insights into the possible performance of AD of lignocellulosic stillage in UASB reactors. As can be seen, up to 80% of COD are removed in the case of molasses and even higher degrees of

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[62] *However, Buswell's equation (13) does not take into account any N contained in the substrate; on the other hand when calculating the COD of organic matter, N is per definition converted to $NH_3$. (see equation (14)). For a substrate containing N the COD removal and the conversion according to Buswell usually differ.*

[63] *For AD C5 sugars are well suited.*

degradation are reached with lignocellulosic stillage. At the same time, very high organic loading rates were maintained (OLR: 10- 36 kg COD/m$^3$d). Actual flowsheeting assumptions are listed in Appendix B.

#### 2.3.10.3 Biogas Upgrading

As outlined in section 2.3.10.2, all the energy in biogas is conserved in $CH_4$ whereas $CO_2$ and all other minor components can be considered as impurities. For the removal of the minor components and $CO_2$ the terms **gas cleaning** and **upgrading** are used, respectively. The final product of gas cleaning and upgrading is pure methane **(bio-methane)** that can be fed into the natural gas grid or sold in gas filling stations[64].

There are various technologies available for gas cleaning and upgrading [Urban *et al.* , 2009, Petersson & Wellinger, 2009] (see Fig. 2-17). Some particularities have to be considered, when biogas originating from AD of lignocellulosic stillage shall be cleaned and upgraded. First, sulfur ($SO_2$ or $H_2SO_4$) used in the pretreatment (see section 2.3.2) probably results in a high content of $H_2S$ in the biogas and second, a very large production scale for AD and biogas upgrading can be expected as a result of the very large scale that is necessary for lignocellulosic ethanol production[65].

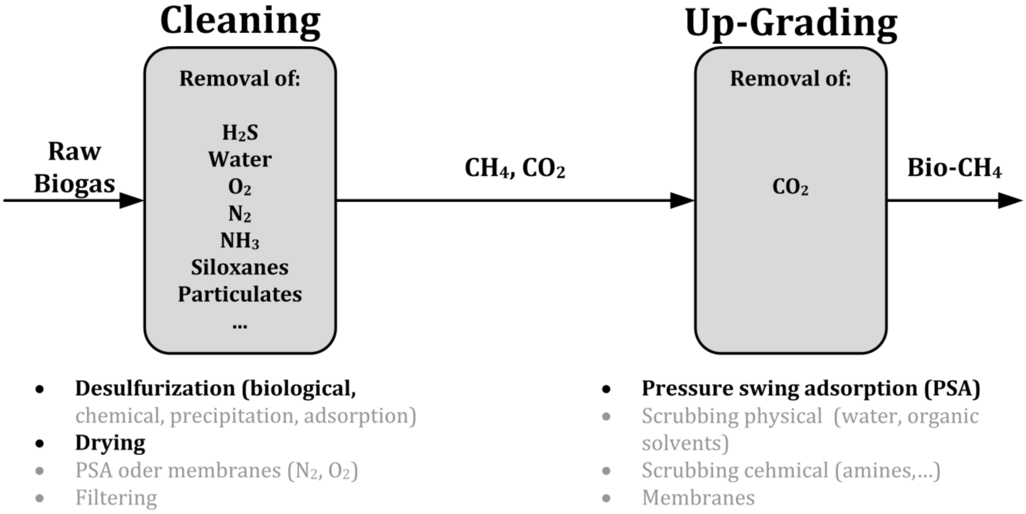

*Fig. 2-17: Some biogas cleaning and up-grading technologies. Technologies in black, bold characters are briefly explained in the text*

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[64] *The actual purity of biomethane depends on the end use. Regulations.*

[65] *Due to economies of scale lignocellulosic ethanol facilities must be very large.*

In the **desulfurization** unit operation, $H_2S$ (originating from reduction of sulfur compounds ($SO_4^{2-}$, $SO_3^{2-}$, S) during AD) is removed. Considering the high $H_2S$ content of the biogas and the large production scale, biological desulfurization is the most suitable technology [Urban *et al.* , 2009]. To avoid the addition of $O_2$ to the biogas stream, a bio-scrubber with external water regeneration is recommendable for biological desulfurization [Urban *et al.* , 2009]. In this type of bio-scrubber the absorption of $H_2S$ in the scrubbing liquid and the microbial oxidation of $H_2S$ (water regeneration) are separated spatially. As a result no undesired $N_2$ or $O_2$ is added to the biogas to be cleaned. The company Paqell provides the required technology under the name **THIOPAQ®**. According to the factsheet, up to 99.9% of $H_2S$ can be removed in very large scale production (150 t Sulfur per day) [paq, 2012]. The raw biogas is rich in $H_2S$ and enters at the bottom of a counter current scrubbing column. In the column $H_2S$ is absorbed in an alkaline solution. The sulfur free product gas leaves the scrubber at the top; the liquid containing the sulfur is fed to a bioreactor in which microbial oxidation (sparging with air) of $H_2S$ to S takes place. After sulfur removal (mechanical methods) the liquid can be reused for absorption. Elemental sulfur obtained as a by-product of the desulfurization unit can be used as fertilizer or pesticide [paq, 2012].

After the biological removal of sulfur the biogas has to be **dried**. To this end, the biogas is compressed and cooled which results in the condensation of water and other condensable gases (e.g. NH3). With this method the water content of biogas can be reduced to less than 0.15 v/v%. Drying of the biogas is very important because condensation in subsequent process steps could cause severe corrosion. The desulfurized and dried biogas can now be up-graded to natural gas quality.

To remove $CO_2$ from the cleaned biogas various options exist (see Fig. 2-17). For smaller volume flows, membranes are a good choice [Makaruk *et al.* , 2010]. However, for the large scale uprgrading of biogas considered in this work, **pressure swing adsorption (PSA)** is advantageous [Petersson & Wellinger, 2009]. Prior to PSA, the $H_2S$ and water content have to be reduced to less than 5 mg/m$^3$ and 0.15 v/v%, respectively [Urban *et al.* , 2009]. The operating principle of PSA was described previously (see section 2.3.8.2), however, when PSA is used for biogas upgrading $CO_2$ is adsorbed (instead of water) and $CH_4$ is used for regeneration (instead of ethanol). $CH_4$ losses[66] can be kept below 2% [Urban *et al.* , 2009]. The waste gas from PSA mainly contains $CO_2$ but also small amounts of lost $CH_4$. In order to avoid $CH_4$-emissions, the waste gas is flared. If there is a combustion unit at the site (see section 2.3.11), the waste gas can be co-fired in this unit. An advantage of PSA compared to other up-grading technologies is the fact, that no chemicals are needed and no waste water is produced. Moreover, the product gas from PSA is obtained at a high pressure, which saves compression energy for grid injection and gas stations. Only electrical energy is

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[66] *Due to i) adsorption and ii) regeneration.*

required and with approx. 0.25 kWh/Nm$^3$ raw gas the specific demand is low[67]. The product gas purity that can be obtained with PSA is >96% [Urban *et al.* , 2009]. Actual flowsheeting assumptions are listed in Appendix B.

### *2.3.11 COMBUSTION OF PROCESS RESIDUES*

Another strategy to make use of the stillage's energy potential is the **combustion** of the organic process residues. The heat released can be used to provide process heat or to run a Rankine cycle. For two reasons, the combustion of process residues is a standard practice in lignocellulosic ethanol production [Sassner *et al.* , 2008, Aden *et al.* , 2002]. First, the stillage contains a lot of energy (see section 2.3.9) which can be used to provide process heat. In this way, the use of other (fossil) energy carriers for process heating can be avoided [Sassner *et al.* , 2008, Aden *et al.* , 2002] and energy self-sufficiency of the production process production[68] can be achieved. A significant reduction of GHG emissions of the production system is the result of this strategy. Second, process residues are burnt because yet no established products and markets exist for these materials. In ethanol production from starchy crops, quite the opposite is the case. Here, process residues are sold as animal food (DDGS) generating a significant share of the overall income of the plant [Kwiatkowski *et al.*, 2006].

Various options exist for the generation of process heat from process residues. After a solid-liquid separation and evaporation of the liquid fraction the combustion of i) the solid fraction only, ii) the solids and the evaporation concentrate or iii) the concentrate only[69] are possible. If necessary, the solids can be dried before the combustion. When biogas is produced through AD of the liquid fraction of the stillage, iv) the biogas can be burned directly together with the separated solids or v) the waste gas from potential upgrading (see section 2.3.10.3) can be co-fired to the separated solids.

For heat utilization, there are also various options available. To provide heat for a chemical process, steam generated in a **steam boiler** is typically used. If only process heat shall be provided, a simple steam boiler is sufficient. In lignocellulosic ethanol production saturated steam at a maximum of 20 bar is sufficient (see sections 2.3.2 and 2.3.9.3); neither superheating of saturated steam nor high pressures are necessary. The amount of organic residues that are incinerated is chosen in a way to match the process heat demand. Solids exceeding this heat demand can be pelletized and used as external fuel; evaporation concentrate can be sold as animal feed or biogas booster [Larsen *et al.*, 2012]. When all the process residues are combusted, the heat that is produced exceeds the process needs (see ***Paper II*** and [Sassner *et al.*, 2008, Aden *et al.*, 2002]. This excess heat

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[67] *That corresponds to less than 5 % of the energy contained in the biogas.*

[68] *As far as heat is concerned.*

[69] *Assuming that a use for the solid fraction exists. Technically this is probably the most challenging option.*

can be used to provide external heat or to generate electricity in a steam turbine. Thereto an **extraction turbine** from which steam is released at the required levels (turbine stages) can be used. There are two types of extraction turbines available. When the condensation of non-extracted steam takes place under vacuum, a so called **extraction condensation turbine** is used. This type of turbine maximizes the electricity output; however, the heat of condensation has to be removed by cooling water. When the condensation of non-extracted steam takes place at higher pressure, the term **extraction back-pressure turbine** is used. With this type of turbine less electricity is obtained, however the heat of condensation can be used for process needs or to provide district heat.

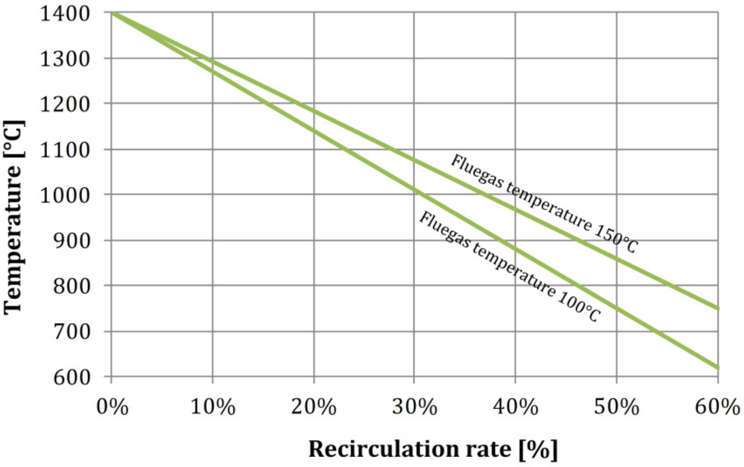

*Fig. 2-18: Reduction of combustion temperature due to fluegas recirculation. Adapted from [Kaltschmitt* et al.*, 2009]*

Regardless of the type of heat utilization, the most important parameters of this process section are the operating temperature of the combustion unit (=hot flue gas temperature), the temperature of the flue gas after heat exchange, the operating parameters of the steam cycle and the efficiencies of electricity generation. In biomass combustion units the maximum allowable temperature is defined by ash melting. This is particularly problematic when straw biomass is used. For instance, ash of maize- and wheat straw melt at 848 °C and 880 °C, respectively, whereas spruce ash only melts at 1340 °C [bio, 2009]. To reduce the temperature in biomass combustion units, flue gas recirculation is a common practice. A part of the cold flue gas[70] is mixed with fresh combustion air. This results in reduced oxygen content and higher amount of inert gases causing a drop of the

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[70] *Cooled down by heat exchange in the steam boiler.*

combustion temperature. As shown in Fig. 2-18, the combustion temperature can thus be regulated by the recirculation rate. Non recycled flue gas leaves the system at atmospheric pressure. Water is normally present as vapor, unless a flue gas condensation system is applied. More information about biomass combustion can be found in specialized textbooks (e.g. [Kaltschmitt *et al.* , 2009]). Actual flowsheeting assumptions for this section are listed in Appendix B.

## 2.4 BY-PRODUCTS IN LIGNOCELLULOSIC ETHANOL PRODUCTION

As outlined in section 2.1.2, the carbohydrate content of lignocellulosic biomass sums up to some 65%. As a result, at least 35% of the biomass fed to the process can not be converted to ethanol. When C5 sugars are not fermented to ethanol (see section 2.3.4) the fraction of non-convertible materials increases to 61% and 42% for straw and spruce, respectively. These figures clearly illustrate the significance that by-product generation plays for the feasibility of lignocellulosic ethanol production. What follows is a list of potential by-products that can be obtained from lignocellulosic process residues[71]:

i. **Heat:** Process residues can be burnt to provide process heat and thereby replace external fuels (see section 2.3.11). Typically, the process heat demand is lower than the energy contained in the process residues (including conversion losses) [Sassner *et al.* , 2008, Aden *et al.* , 2002]. The excess thermal energy can therefore be used for external applications, such as a co-located production facility or a district heating grid.
ii. **Electricity:** Another option to use the excess energy contained in the process residues is the generation of electricity for process and external uses (see section 2.3.11). The CHP system can also be designed, to provide both excess heat and excess electricity (see section 2.3.11).
iii. **Pellets:** After a drying step, the lignin rich solid fraction can be pelletized (see section 2.3.11). The solid energy carrier that is obtained has a high energy density and can be converted in a temporally and locally decoupled process. This decoupling increases the flexibility of the energy system. Depending on the type of the furnace that is used for conversion (industrial incineration vs. domestic stoves) and on the type of the feedstock (straw vs. spruce), it may be necessary to remove undesired inorganic compounds (sulfur and ash) by means of a washing step.
iv. **C5 Molasses (straw only, no fermentation of C5 sugars):** The concentrated liquid fraction that is obtained after a solid-liquid separation and subsequent evaporation contains a high amount of soluble C5 sugars.

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[71] *This list does not claim to be exhaustive.*

These so-called C5 molasses[72] can be used as animal feed, as a biogas booster (co-feeding in conventional biogas plants) [Larsen *et al.* , 2008, Larsen *et al.* , 2012] or as a sugar source for various biotechnological processes.

v. **Biogas or Biomethane:** The whole stillage or a part thereof can be subjected to anaerobic digestion (see section 2.3.10). Various options exist to utilize the resulting biogas: i) combustion to provide process heat, ii) conversion to electricity in a gas engine or turbine, upgrading to biomethane and iii) subsequent injection into the gas grid or iv) supply of a gas station.

vi. **Carbon dioxide:** When sugars are fermented to ethanol an equimolar amount of $CO_2$ is produced (see section 2.3.4). Likewise, in yeast and enzyme production a part of the substrate is converted to $CO_2$ (see sections 2.3.6 and 2.3.5). In contrast to a combustion process, the off-gas resulting from these biochemical processes contains $CO_2$ in almost pure form. As a result, the efforts necessary to provide high-purity $CO_2$ is relatively small. Potential uses for the purified $CO_2$ include, refrigeration systems, food packaging, beverages, the production of chemicals (e.g. urea) and many more [Mazzotti *et al.* , 2005].

vii. **Synthesis gas:** Gasification is another strategy to utilize the process residues from lignocellulosic ethanol production [Morandin *et al.* , 2011, Zhang *et al.* , 2009]. The synthesis gas obtained can be used in an integrated gasification combined cycle, providing electricity and heat, for fermentation to various products [Werpy *et al.* , 2004] or for chemical synthesis.

viii. **Materials:** The unconverted sugars as well as the synthesis gas and the lignin fraction can serve as a basis for a whole range of materials [Werpy *et al.* , 2004, Holladay *et al.* , 2007]. Various biorefinery concepts can be developed based on these so-called platform chemicals (see section 1.2.).

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[72] *When the separation is performed directly after the pretreatment the term molasses is correct, whereas the term vinasses is most suitable for the liquid fraction that is obtained after fermentation and a solid-liquid separation [Jacques* et al.*, 2003].*

# 3 METHODOLOGY

In section 2 the technology of ethanol production from lignocellulosic biomass was reviewed and the most relevant process parameters necessary for process modeling are summarized. This detailed literature review provides the basis for the further steps in the workflow. This workflow is presented in this section and is schematized in Fig. 3-1. In section 3.1 thirteen selected concepts for the production of lignocellulosic ethanol are developed and presented. Next, in section 3.2, the methodology for process simulation of these concepts is briefly explained. Then, in section 3.3, the derivation and application of options for process heat integration are explained. And finally, in section 3.4 the methods for technology validation of the production concepts are briefly discussed.

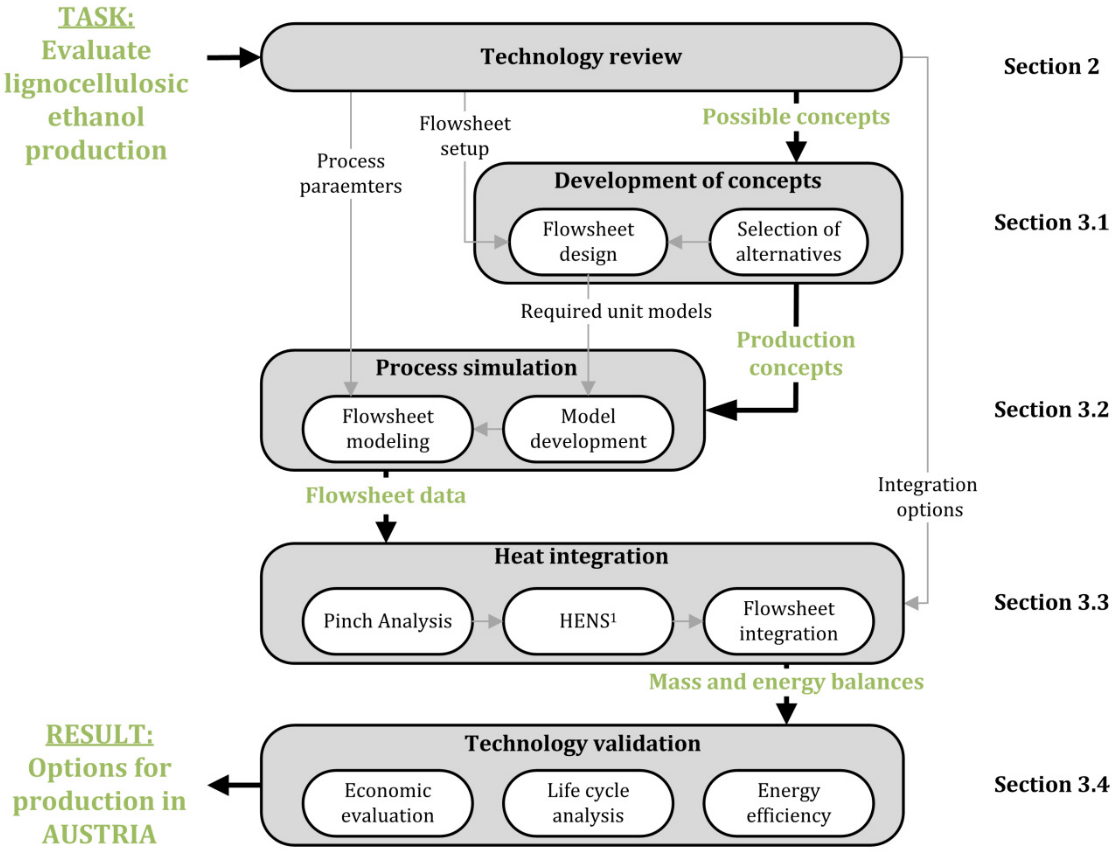

*Fig. 3-1: Methodological approach of this work. $^{1}$...Heat exchanger network synthesis*

As can be seen, data obtained from the literature review is used in various steps of the workflow. First, that data is used for the development of production concepts and for flowsheet design (i.e. which unit operations are used and how these unit operations are connected in the production process). Then process parameters for flowsheet simulations are obtained from the technology review. And finally, options for process integration are derived from the literature review.

It must be mentioned that Fig. 3-1 is a simplified, linear representation of the actual procedure. In reality, many of the single steps are intertwined with each other. This results in an iterative character of the workflow. In several steps of the workflow information is obtained that makes it necessary to return to previous steps. For example, flowsheet data which is only available after process simulation may lead to an elimination of certain production concepts whereas insights gained during process integration may lead to the result that additional production concepts have to be considered (see ***Paper I*** vs. ***Paper* V**). But also after the production concepts are fixed, iteration can be necessary. For example, information obtained during process integration can lead to the conclusion that flowsheet design can be improved (see ***Paper II***). This iterative character of the workflow is not shown in Fig. 3-1 for simplicity reasons.

## 3.1 DEVELOPMENT OF PRODUCTION CONCEPTS

As can be concluded from sections 1 and 2, a wide range of technological options exists for the production of ethanol from lignocellulosic biomass. It is impossible to consider all these technological options in detail; therefore a selection of production alternatives is necessary when the technology perspectives for Austria shall be assessed. The selection process, flowsheet design of the selected alternatives as well the resulting production concepts are shortly presented in this chapter. The selected production concepts will then be developed and investigated in detail using process simulation (see section 3.2), process heat integration (see section 3.3) and technology validation (see section 3.4).

### *3.1.1 SELECTION OF ALTERNATIVES*

To ensure sustainability of biofuel production the following criteria were applied in the selection procedure:

i. **Expected economic feasibility:** In the long run, lignocellulosic ethanol can only play a role in Austria's energy system when it's is economically feasible. Therefore those conversion technologies were selected for which highest ethanol yield and lowest investment and operating cost can be expected. Also the plant capacity used in the analysis was fixed based on economic feasibility (economies of scale principle).

ii. **Biomass availability in Austria:** Only those types of lignocellulosic biomass shall be considered in the analysis whose potential is large enough (see section 2.1) to supply at least one plant of the fixed capacity. By applying this criterion, energy security, which is mandated for sustainable bioenergy production (see section 1.1), is guaranteed automatically.

iii. **Technological maturity:** Many of the conversion technologies described in section 2.3 have only been tested in lab-scale. For these technologies the performance in industrial production is highly uncertain. Moreover for these technologies potential improvements through years of R&D are difficult to predict which makes a comparison with more mature technologies difficult. Therefore only technologies are considered that have been tested at least in pilot scale.

iv. **Energy self sufficiency:** Energy self sufficiency in the production process has the potential to improve both the economic and the environmental performance of the technology. Therefore, this principle is applied for all concepts under investigation.

v. **Complete utilization of energy and material potential:** A complete utilization of the biomass' energetic and material potential is beneficial when aiming at a high conversion efficiency and acceptable economic and environmental performance. That part of the biomass that can not be converted to ethanol shall therefore be used to provide process energy (see item iv) or material or energy by-products.

vi. **Legal situation in Austria:** Presently it is uncertain whether a genetically modified organism (GMO) can be used in an industrial production facility in Austria. Therefore those technologies which do not employ GMO's shall be treated with preference (see section 2.3.4). However, to show the potential of C5 fermentation[73], this technology is not completely excluded from the analysis.

### *3.1.2 FLOWSHEET DESIGN*

Many large research teams have dedicated years of R&D to process and flowsheet design of lignocellulosic ethanol production. Therefore, no entirely new flowsheet designs are developed in this work. Instead flowsheet designs are derived from the literature review (see also Fig. 3-1). In particular the flowsheet designs in this work are based on the work performed at the US National Renewable Energy Laboratory (NREL) [Aden *et al.* , 2002, Humbird *et al.* , 2011], at the Department of Chemical Engineering at the Lund University,

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[73] *As outlined in section 2.3.4, fermentation of C5 sugars requires GMO's.*

Sweden [Sassner *et al.* , 2006, Sassner, 2007, Sassner *et al.* , 2008, Wingren *et al.* , 2003, Wingren *et al.* , 2004, Wingren *et al.* , 2008] and by Inbicon [Larsen *et al.* , 2008].

### *3.1.3 PRODUCTION CONCEPTS*

As a result of applying the above described procedure thirteen production concepts were developed. The concepts share the following characteristics:

- i. **Biomass types** softwood (spruce) or straw are considered only.
- ii. **Ethanol production capacity** of the plant is fixed at 100’000 t per year.
- iii. The following **technologies** were considered for all concepts:
    - a. Steam pretreatment with addition of $SO_2$. No detoxification.
    - b. Enzymatic hydrolysis.
    - c. On site enzyme production on pretreated biomass.
    - d. SS(C)F of the whole slurry.
    - e. Product recovery using multicolumn distillation and PSA.
    - f. Solid – liquid separation of the stillage and drying of the solid fraction.
    - g. Combustion of process residues.

In Table 19 the resulting production concepts are summarized. As can be seen the enumerated concepts differ in i) the type of biomass (10 concepts are considered for straw and 3 concepts for softwood), ii) the utilization of sugars in SSF iii) the by-products obtained from the non-fermentable compounds and iv) the allocation process electricity.

*Table 19: Summary of concepts under investigation*

| No. | Biomass | Fermentation | By-products from stillage | | Allocation of electricity |
|---|---|---|---|---|---|
| 1 | Straw | C6 | Electricity | | produced on-site |
| 2 | Straw | C6+C5 | Electricity | | produced on-site |
| 3 | Straw | C6 | Electricity | District Heat | produced on-site |
| 4 | Straw | C6 | Pellets | | purchased |
| 5 | Straw | C6+C5 | Pellets | | purchased |
| 6 | Straw | C6 | Pellets | District Heat | purchased |
| 7 | Straw | C6 | C5 Molasses | Pellets | purchased |
| 8 | Straw | C6, HWIS[1] | C5 Molasses | Pellets | purchased |
| 9 | Straw | C6 | C5 Molasses | District Heat | purchased |
| 10 | Straw | C6 | Biomethane | Electricity | produced on-site |
| 11 | Wood | C6 | Electricity | | produced on-site |
| 12 | Wood | C6 | Pellets | | purchased |
| 13 | Wood | C6 | Biomethane | Electricity | purchased |

*[1] HWIS...Fermentation is performed with a higher content of solids which requires a solid – liquid separation prior to SSF*

Fig. 3-2 is a flowsheet-like summary of the 13 production concepts listed in Table 19. As can be seen, all concepts but one[74] are identical regarding the type and arrangement of the unit operations steam explosion, enzyme – and yeast production, SSF, distillation, PSA and solid-liquid separation. As mentioned above, in all concepts process heat (steam) is provided by burning part of the stillage. As a result no additional fossil fuels have to be employed to heat the process.

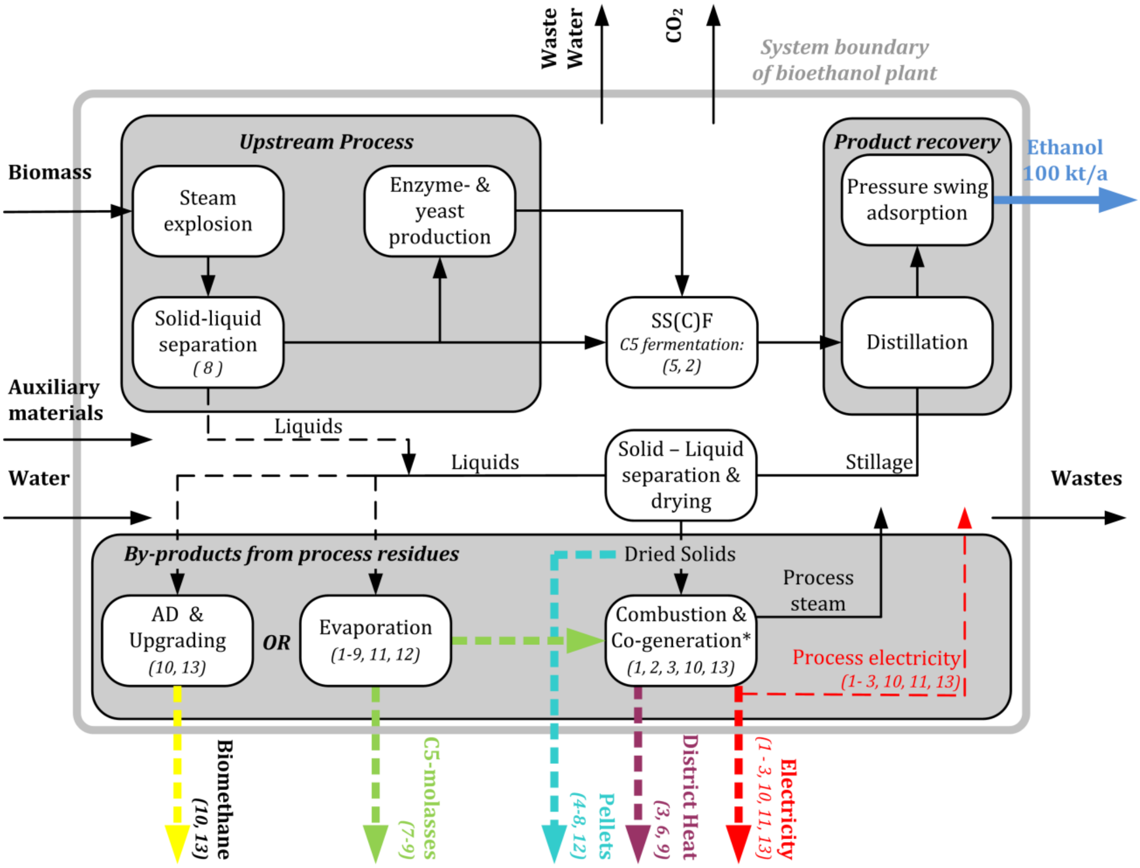

*Fig. 3-2: Flowsheet-like scheme summarizing the 13 production concepts. Solid lines are used for streams included in all concepts. Dashed lines are used for streams included in enumerated concepts (concept number in brackets). *enumerated concepts include co-generation. Adapted from:* ***Paper V***

For some concepts process electricity is also generated on-site by converting the stillage to heat and electricity using a Rankine cycle (concepts 1-3, 10, 11, 13). These concepts are completely energy self sufficient (heat and electricity) and excess electricity is a by-

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[74] *Concept number 8 slightly differs from the other concepts. Here the fermentation of C6 sugars is performed at a higher solid content (HWIS). To avoid inhibition in SSF, a solid – liquid separation after the pretreatment and prior to SSF is necessary.*

product that can be sold to the grid. In contrast, for those concepts that do not produce electricity on-site (4-9, 12), process electricity has to be purchased.

As previously mentioned all mass and energy balances are calculated for an annual ethanol output of 100’000 t and an operating time of 8000 h.

A more detailed description of the production concepts can be found in ***Papers I*** and ***V***. It is important to note that the concepts presented in ***Paper I*** differ from the finalized set of concepts presented in ***Paper V***. This difference is based on the fact that ***Paper I*** was written at the beginning of the workflow (see Figure Fig. 3-1) prior to any flowsheet modeling or a detailed investigation of the Austrian biomass potential. During the course of the work (iterative character of the workflow, see above) some of the concepts from ***Paper I*** were identified as infeasible or not relevant and dismissed from the analysis whereas other concepts were added or modified. In ***Paper V***, the finalized set of concepts is presented together with the results of technology validation.

## 3.2 PROCESS SIMULATION

Process simulation is used to obtain detailed mass and energy balances for the production concepts described in section 3.1 (see also Fig. 3-1). For that purpose the equation oriented, steady state flowsheet simulation software **IPSEpro** is used. In Fig. 3-3 IPSEpros’s operating principle is schematized. The model development using IPSEpro’s **Model Development Kit (MDK)** is discussed in section 3.2.1; flowsheet modeling in IPSEpro’s **Process Simulation Environment (PSE)** is outlined in section 3.2.2.

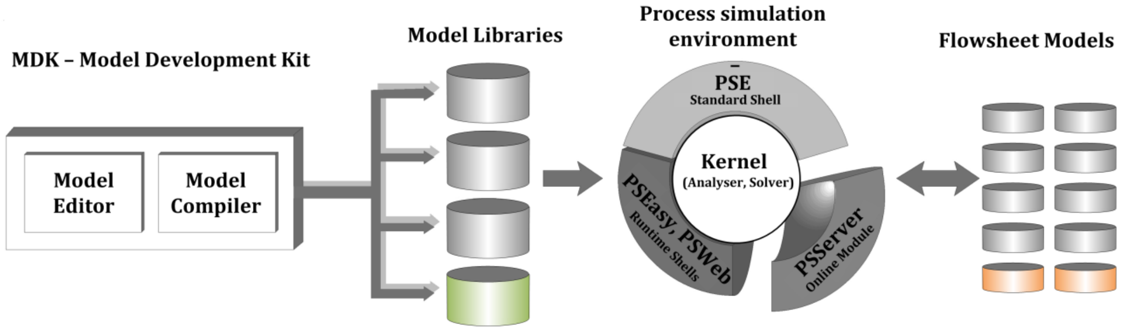

*Fig. 3-3: Operating principle and structure of the flowsheeting software IPSEpro. A new model library (green) was developed to perform flowsheet simulations (orange) of the production concepts*

### *3.2.1 MODEL DEVELOPMENT*

IPSEpro was originally developed for the simulation of power plants [Perz & Bergmann, 2003], however, its open and flexible structure allows the development of new model libraries. The model development carried out within this work is based on previous developments at the Vienna University of Technology's Institute of Chemical Engineering. Extending IPSEpro's standard library for power plant simulations (**APP_Lib**), Pfeffer [Pfeffer, 2006] developed a model library that contains i) the chemical species and ii) the basic unit operations of ethanol production from starchy materials. Schausberger [Schausberger *et al.* , 2010] modified and improved this latter bioethanol library to create the **APP_BioLib**. The library developments within this work are based on the **APP_BioLib** and result in a new model library named **APP_BioLib_Ligno**.

In principle there exist **global**, **connection** and **unit** objects in IPSEpro [Perz & Bergmann, 2003, Pfeffer, 2006]. To obtain the **APP_BioLib_Ligno** modification and improvements[75] on each object level were necessary. On the **global** level, the composition of chemical species and their properties are managed [Perz & Bergmann, 2003]. Here the following changes were made:

- The **Biofuel global** was developed. New liquid components can now be balanced.
- The **Weender global** was extended to include additional biomass components and the option to automatically compute the specific volume was added.

On the **connection** level, stream data is handled [Perz & Bergmann, 2003]. Here the following features were added to the **biostream** object:

- The variable **wis** (water insoluble solids) was added.
- The enthalpy of biomass **h(t)**[76] is calculated based on an empiric relationship.

As the name implies, the **unit** level is used to manage unit operations [Perz & Bergmann, 2003]. Here, the largest number of modifications were necessary because many of the unit operations described in section 2.3 had to be programmed. Table 20 summarizes newly developed units and modifications made to existing units within the course of this work.

A description and documentation of the modifications that lead to the **APP_BioLib_Ligno** is given in Appendix A.

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[75] *With respect to the* ***APP_BioLib***

[76] *And its derivative* $c_p=dh/dt$

*Table 20: Summary of new unit operations modifications in the* ***APP_BioLib_Ligno*** *library*

| Unit Name in IPSEpro | Physical unit operation | Work |
|---|---|---|
| bf_aerobic_stage | Aerobic water treatment | New unit |
| bf_bioreactor | Aerobic production of yeast | New unit |
| bf_ch4_fermenter | Anaerobic digestor | Modifications |
| bf_converter | Conversion without phyiscal meaning | New unit |
| bf_enzymeproduction | Enzymeproduction | New unit |
| bf_etoh_adsorber | PSA for ethanol recovery | Modifications |
| bf_etoh_fermenter | Ethanolfermentation | Modifications |
| bf_etoh_cellulosedigestion | Enzymatic hydrolysis of cellulose | Modifications |
| bf_evap, bf_flash | Evaporation and Flash unit | Modifications |
| bf_filterpress | Filterpress | New unit |
| bf_heatsource | Heater | New unit |
| bf_liquid_hot_water | Liquid hot water pretreatment | New unit |
| bf_COD_biofuel | Monitor for chemical oxygen demand | New unit |
| bf_COD_elementary | Monitor for chemical oxygen demand | New unit |
| bf_monitor_HV | Monitor for heating value | New unit |
| bf_size_reduction | Size reduction | New unit |
| bf_sludge_separator | Water treatment unit | New unit |
| bf_steam_dryer | Superheated steam dryer | New unit |
| bf_steam_explosion | Steam explosion | Modifications |

### *3.2.2 FLOWSHEET MODELING*

The newly developed **APP_BioLib_Ligno** is designed for flowsheet simulations of the thirteen production concepts described in section 3.1. In IPSEpro, these flowsheet simulations are performed in the **Process Simulation Environment (PSE)** program module (see Fig. 3-3). From a converged flowsheet simulation data can be extracted or exported for further analysis and process validation.

In this work, **flowsheet modeling** and **process integration** (section 3.3) are strongly intertwined, i.e. data from flowsheet simulations is used in process integration and vice versa. In Fig. 3-4, the intertwined workflow during process simulation and process heat integration is shown. First, a non-integrated flowsheet model of the production process is developed in IPSEpro. Flowsheet data is extracted and used for the first step of process integration: **pinch analysis** (see section 3.3). Based on the result of the pinch analysis, modifications to the flowsheet design (i.e. distillation or evaporation section, see ***Paper II***) are made if necessary. When process design and pinch analysis are completed, a **heat exchanger network** is developed (see section 3.3). This network is again implemented in IPSEpro to obtain a fully integrated flowsheet of the respective production concept. The resulting mass and energy balances of the production concept are then used for process analysis and validation.

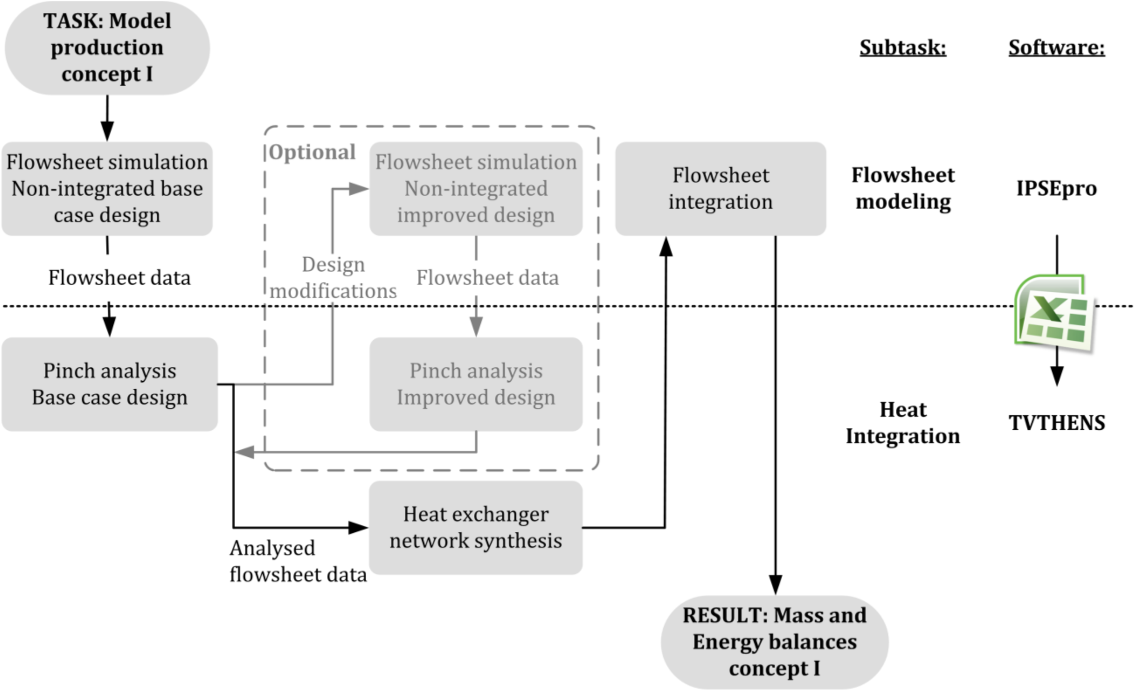

*Fig. 3-4: Detailed workflow during flowsheet modeling and process heat integration. Adapted from* ***Paper II***

In ***Paper III*** and ***Paper IV***, the results of process simulation are presented and analyzed for selected production concepts. Appendix B contains flowsheet assumptions; the mass and energy balances for all the production concepts are summarized in Appendix C. The flowsheets can be found in Appendix D.

## 3.3 HEAT INTEGRATION

In any chemical plant there are streams that require heating (i.e. cold process streams) and other streams that require cooling (i.e. hot process streams). This heating and cooling is provided by hot and cold utilities (e.g. steam and cooling water). However, heating for a cold process stream can also be provided by a hot process stream which is in turn cooled. As a result of this process-process heat exchange, i.e. **process heat integration**, both the hot and the cold utility consumption of the process are reduced. This reduction of utility consumption goes hand in hand with i) a reduction of the amount and costs of external fuels, ii) an increase in process efficiency and iii) a reduction of $CO_2$ emissions of the process[77]. The significance of heat integration, in particular in biofuel production, is therefore evident.

Within this work two standard methods are applied for process heat integration (see also Fig. 3-1 and section 3.2). Namely these are: i) **pinch analysis** and ii) **heat exchanger network synthesis (HENS)**. However, before applying these methods, options for heat integration were identified by reviewing the literature (see also Fig. 3-1). As a result of this review, the energy intensive unit operations in the process were designed to have a high potential for heat recovery. To be specific the following design choices were made:

i. **Steam pretreatment** (see section 2.3.2.2): The flashing after steam pretreatment is performed in two steps, at **medium pressure** (**MP**, ca. 4 bar) and at **atmospheric pressure (AP)**. Secondary steam is obtained at the respective levels [Wingren *et al.*, 2003, Sassner *et al.*, 2008]. Especially MP steam is valuable and can be used for heat integration.
ii. **Superheated steam drying** (see section 2.3.9.3): This drying technology is used because of its high potential for heat integration. The dryer is operated at MP level to yield MP secondary steam. This steam can be used to heat other parts of the process [Sassner *et al.*, 2008].
iii. **Distillation setup** (see section 2.3.8.1): A thermally integrated multi column setup was chosen. In particular, the design with two parallel stripper columns and one vacuum rectifier column was implemented [Wingren *et al.*, 2008]. The setup is designed to require heat at the MP level, which can partly be provided from secondary steam.
iv. **Evaporation setup** (see section 2.3.9.2): To reduce the heat demand in the evaporation section, a multi stage evaporation system is implemented. A 5 stage co-current setup was chosen. Just as the distillation section, the system is designed to require heat at the MP level.

With these design choices made, secondary steam obtained from steam pretreatment and superheated steam drying unit operations can be used to heat the distillation and evaporation section. These design choices are implemented to create non-integrated flowsheet model of the process (see section 3.2). The data obtained from a converged simulation of this model is used for pinch analysis and heat exchanger network synthesis.

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[77] *For the energy self-sufficient processes considered in this work (see section 3.1), the reduction of utility results in an increase of by-products that can be obtained from non-fermentable compounds of the biomass. This also positively affects process economics, efficiency and emissions.*

### 3.3.1 PINCH ANALYSIS

Pinch analysis is systematic method to reveal options for heat recovery in a process. As a result of pinch analysis, the **hot** and **cold energy target**[78] of a process are obtained [Kemp, 2007]. These targets are a benchmark for the utility demand of a process because they represent the thermodynamic minimum for a fixed design and fixed **minimum temperature difference ΔTmin**[79]. Therefore, the energy targets of different process designs can be used to determine the most efficient design option. Details about pinch analysis fundamentals can be found in dedicated textbooks [Smith, 2005, Kemp, 2007].

Within this work pinch analysis was performed using **TVTHENS** [Modarresi, 2013]. TVTHENS is a software package for process heat integration that was developed at the Vienna University of Technology's Institute of Chemical Engineering. TVTHENS was programmed using the software program "Mathematica" and contains program modules for pinch analysis and heat exchanger network synthesis.

As indicated in Fig. 3-4, thermal stream data is extracted from a converged flowsheet simulation in IPSEpro and exported to MS Excel to be used as input for pinch analysis in TVTHENS. Throughout this work pinch analysis is performed with a $\Delta T_{min}$ of 10 °C. More details about pinch analysis methodology can be found in ***Paper II.***

In this work, the results of pinch analysis are used in two ways. First, the process design is checked for potential improvements. In particular, pinch analysis is used to analyze and improve the design of the energy intensive multi-stage unit operations distillation and evaporation (see ***Paper II***). Second, the energy targets obtained from pinch analysis serve as a benchmark for the fully integrated flowsheets. These fully integrated flowsheets are obtained after heat exchanger network synthesis (see section 3.3.2).

### 3.3.2 HEAT EXCHANGER NETWORK SYNTHESIS

After pinch analysis the flowsheet design is fixed (and the energy targets are calculated). Now, a heat exchanger network is synthesized for this fixed design. The heat exchanger network resembles the true utility demand of a process whereas the energy targets obtained from pinch analysis are the thermodynamic minimum (see section 3.3.1). This thermodynamic minimum can only be achieved with a very large number of heat exchangers which is economically infeasible. Thus, in heat exchanger network synthesis (HENS) the economic optimum of a capital energy trade off problem has to be found.

To perform HENS for a given production concept, analyzed flowsheet data is exported from IPSEpro. HENS calculations are then performed with the respective program module

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[78] *Sometimes the synonyms **energy targets** or **minimum utility requirement** are used.*

[79] *$\Delta T_{min}$ is the minimal temperature difference that is allowed for heat exchange between two streams.*

of "TVTHENS". This program module is capable to handle process streams that undergo both sensible and latent heat changes (e.g. streams in the multi stage evaporation) and utilizes an extended mixed integer linear programming model proposed by Ponce-Ortega [Ponce-Ortega *et al.* , 2008]. This model is based on the superstructure formulated by Yee and Grossmann [Yee & Grossmann, 1990] in which the total annual cost including utility and heat exchanger costs is minimized. The network synthesis was performed with for a $\Delta T_{min}$ of 10 °C. In order to keep the network simple, stream splitting was excluded in the network synthesis. More information about the HENS methodology can be found in ***Paper II***.

### *3.3.3 FLOWSHEET INTEGRATION*

The heat exchanger network obtained from calculations with TVTHENS (section 3.3.2) is checked for plausibility and implemented in IPSEpro (see Fig. 3-4). With the network implemented, the utility demand of the process is fixed. Now, the utility system (steam or co-generation from process residues and cooling system) can be completed and the mass and energy balances of the process can be closed. In this context it is important to remember that for all concepts considered in this work process residues are used for two purposes: i) generation of process heat and ii) generation of material and energy by-products. Therefore, the amount of by-products for a certain concept can only be calculated when the heat exchanger network (which defines the hot utility requirement) is implemented.

The above described procedure of flowsheet modeling and heat integration (see also Fig. 3-4) was performed for the thirteen production concepts under investigation (see section 3.1.3). However, some concepts are very similar or identical in the core process. For these concepts it is not necessary to individually apply the heat integration procedure. Instead these concepts share the same heat exchanger network and have the same utility requirement. Thus, six different networks suffice for the thirteen production concepts under investigation (see also ***Paper V***). As a result of flowsheet integration the mass and energy balances of the fully integrated concepts are obtained. This data forms the basis for any further analysis which is described in the following section 3.4.

## 3.4 TECHNOLOGY VALIDATION

In sections 3.1, 3.2 and 3.3 the methodology for concept development, process simulation and heat integration were explained. As a result of applying this methodology the mass and energy balances for the 13 production concepts are obtained. These balances serve as a basis to assess the production concepts using the parameters and methods described in the following sections.

### *3.4.1 ENERGY EFFICIENCY*

The **energy efficiency η** of an energy conversion technology is defined as the sum of all usable energy outputs divided by the sum of all energy inputs [Pehnt, 2010]. For continuous production processes energy flows (symbol Ė, SI unit W), are used instead of energy (symbol E, SI unit J). Considering the different forms of usable energy, one can distinguish between i) material related energy flow, ii) electrical power and iii) heat flow that enter or leave the process. The general definition of energy efficiency thus obtained is expressed in equation (17).

$$\eta = \frac{\sum \dot{E}_{out}}{\sum \dot{E}_{in}} = \frac{\sum \dot{m}_{i,out} * LHV_{i,out} + P_{el,out} + \dot{Q}_{out}}{\sum \dot{m}_{i,in} * LHV_{j,in} + P_{el,in} + \dot{Q}_{in}} \qquad \text{(17) General definition of energy efficiency } \eta \text{ of a continuous process}$$

*$_{i,j}$...Indices for materials leaving and enterign the system, LHV stands for lower heating value*

To calculate the energy efficiency of the production concepts under investigation, some specifics have to be considered:

Lignocellulosic biomass (wood and straw) and process electricity[80] are the only energy inputs included in the calculation. Process heat is always provided within the system boundaries and other material related energy inputs are very small compared to the energy input through the biomass[81]. These inputs are therefore neglected when calculating the energy efficiency.

The following energy outputs are included: i) the main product ethanol, ii) the material by-products pellets, C5 molasses and biomethane, iii) excess electricity [82]and iv) district heat. The energy efficiency based on the specified usable energy in- and outputs is expressed in equation (18) and will be used throughout this work.

$$\eta = \frac{\sum \dot{m}_{Product\ i} * LHV_{Product\ i} + P_{el,out} + \dot{Q}_{District\ Heat}}{\dot{m}_{Biomass} * LHV_{Biomass} + P_{el,in}} \qquad \text{(18) Definition of energy efficiency } \eta \text{ used in this work}$$

It is important to note, that depending on the production concept, some of the terms are equal to zero and therefore do not contribute to the process energy efficiency. Moreover it is worth noting that in this definition of energy efficiency, the ethanol plant boundareies are applied as system boundary; therefore conversion losses that occur before the ethanol

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*[80] If applicable; only some of the concepts require process electricity as energy input.*

*[81] Mass flow as well as the lower heating values (LHV) of plant auxiliaries (beet molasses, corn steep, diammoniumphosphate, etc. ) are very small compared to the mass flow and LHV of biomass. Some auxiliaries are provided as aqeuous solutions, for theses materials the LHV can even become negative.*

*[82] For those concepts that supply electricity only the amount exceeding the process needs is counted.*

plant (e.g. photosynthetic efficiency) or during the conversion to end energy are not taken into account (e.g. combustion of ethanol in the car's engine, pellet combustion, heat losses in the district heating grid…). Neither does this definition of efficiency consider the different qualities of the different energy products (e.g. electricity vs. district heat). For that purpose, exergy analysis should be applied [Modarresi *et al.* , 2012]. However, the used definition of energy efficiency is suitable because i) the focus of the analysis is the conversion process and ii) the end use of some of the end-products (e.g. pellets, biomethane, C5 molasses) is uncertain. ***In Paper III***, and ***Paper IV*** energy efficiency for some concepts (straw, biomethane production) are calculated. In section III, the energy efficiency for all concepts is summarized.

#### 3.4.1.1 Lower heating values

To calculate the energy efficiencies of the production concepts as described above, the lower heating values (LHV) of the different input and output materials have to be known. For ethanol a literature value of 26.9 MJ/kg was used [Larsen *et al.* , 2009]. The LHV of biomethane (47.5 MJ/kg) was taken from IPSEpro's database. For consistency reasons, the Lower heating values of all biomass streams, i.e. the substrates wood and straw as well as the process residues pellets and C5 molasses, were calculated using the PLS Model from [Friedl *et al.* , 2005]. This model calculates the higher heating value (HHV) based on elementary compositions of a biomass sample. When this model is used, the HHV has to be converted to LHV. A corresponding unit operation was developed in IPSEpro (see Appendix A).

### *3.4.2 LIFE CYCLE ANALYSIS*

The mass and energy balances of the integrated flowsheets are used as input for life cycle analysis (LCA). As outlined in section 1.4, LCA calculations were not performed by the author but by partners at JOANNEUM RESEARCH. However, to give a full picture of the technology a brief description of the methodology and the most important results obtained are included in this work (***Paper V***).

Life cycle greenhouse gas (GHG) assessment can be used to calculate the potential environmental impact of ethanol produced from lignocellulosic biomass. There exist other methodologies, such as the sustainable process index, to determine the environmental impact and sustainability of technological systems in general and bioethanol production in particular [Gwehenberger *et al.* , 2007]. Nonetheless, within this work LCA is used due to the paramount significance of greenhouse gas emissions in the transport and energy sectors. It must be mentioned that other environmental and sustainability aspects, such as soil quality, food security, land use, energy security & self sufficiency (see section 1.1), are not neglected but covered implicitly: i) due to the selection criteria in section 3.1.1, ii) due to assumptions applied in flowsheet and life cycle modeling. As far as economic aspects of sustainability are concerned, the projected fuel cost is explicitly dealt with in section 3.4.3.

When calculating the mass and energy balances for the production concepts, the ethanol conversion plant's physical boundaries are identical to the system boundaries. As the name implies, the system boundaries have to be expanded in life cycle analysis. Here, GHG emissions from all stages of the bioethanol process chain are considered ("from well to wheel"). The so formed bioethanol system includes:

i. Production, collection and transport of biomass
ii. Bioethanol production plant and operating materials
iii. Bioethanol distribution and use in vehicles
iv. Construction of the vehicle
v. Use of by-products
vi. Disposal of wastes

For all these steps the emissions of the greenhouse gases $CO_2$, $N_2O$ and $CH_4$ are calculated and converted to $CO_2$ equivalents ($CO_2$eq) taking into account the different global warming potential. The results are reported as kilotons $CO_2$eq per year.

The absolute GHG emissions generated in the production of ethanol from lignocellulosic biomass are difficult to interpret. Following a typical strategy to overcome this difficulty [Boerjesson, 2009], the GHG emissions are compared with reference systems that provide the same amount of energy services and by-products. For each bioethanol system two types of reference systems were defined:

i. **A fossil reference system** in which all energy products are derived from fossil resources (e.g. ethanol is replaced by gasoline, the by-products electricity and heat are provided by a CHP plant using natural gas etc.). This reference system can be used for comparison with the present status in Austria: an energy system dominated by fossil energy carriers.
ii. **A renewable reference system** in which only ethanol is replaced with fossil resources (gasoline), whereas all by-products are replaced with renewable by-products (e.g. a straw fired CHP plant). A comparison with this reference system shows the sole effect of replacing gasoline with ethanol. Any GHG emission credits through renewable by-products are not counted using this reference system.

As for the ethanol systems, the GHG emissions of the reference systems are calculated on a life cycle basis and therefore include all emissions associated with raw material extraction, transport, refinement and use. To illustrate the principle, Fig. 3-5 shows one selected bioethanol system and the respective fossil reference system. As can be seen, the same amount of energy services (transportation, heat and electricity) are provided by the two systems.

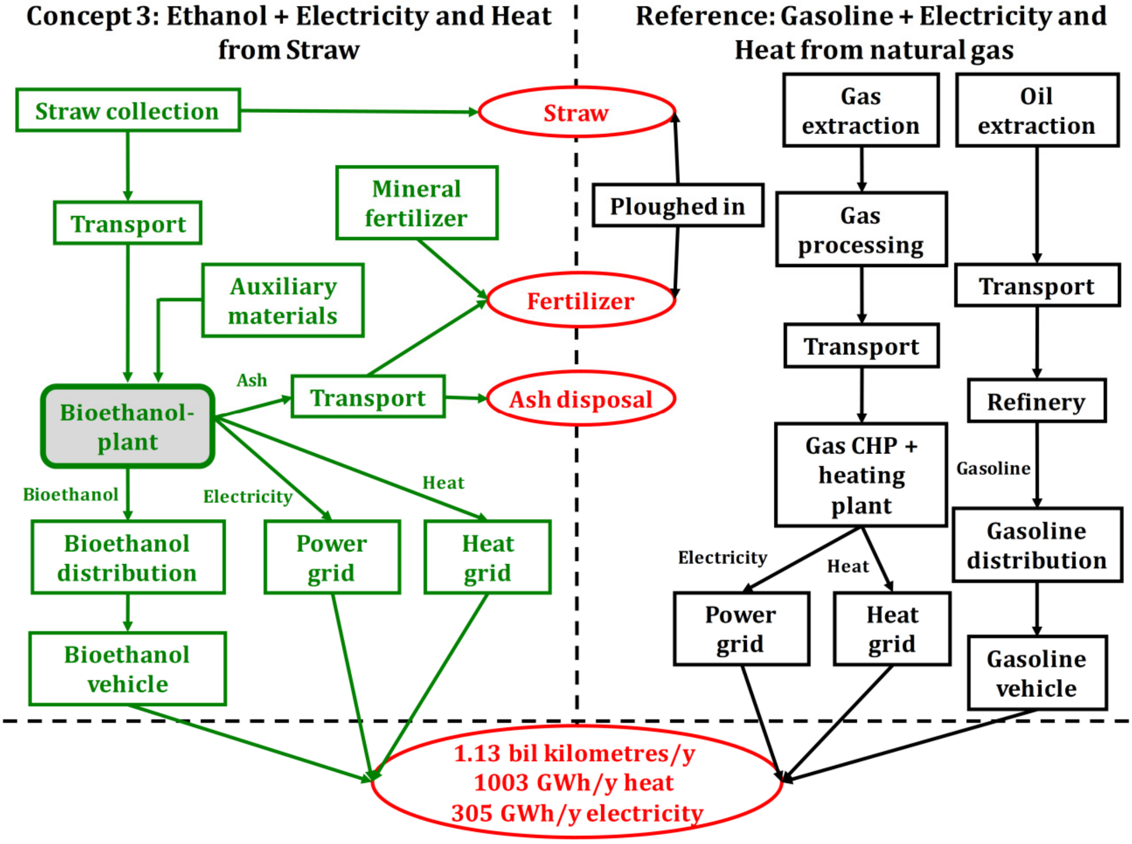

*Fig. 3-5: All stages considered in LCA. One selected bioethanol production system and the respective fossil reference system is shown. Adapted from* **Paper V**

As a result of LCA, detailed GHG emissions of each step of the bioethanol system and the GHG mitigation potential with respect to the reference systems (in %) are obtained for the 13 production concepts. More details about LCA methodology and results can be found in ***Paper V*** and particularly in the final report of the research project [Könighofer *et al.* , 2012].

### *3.4.3 ECONOMIC ASSESSMENT*

The mass balances of the integrated flowsheets are used as a basis to assess the economic performance of lignocellulosic ethanol production. As outlined in section 1.4, the economic assessment was not performed by the author but by partners at JOANNEUM RESEARCH.

However, to give a full picture of the technology a brief description of the methodology and the most important results obtained are included in this work (***Paper V***).

Static cost comparison method is employed to assess the economic performance of the 13 production concepts. Using this method annual costs are calculated considering the following contributions:

1. **Capital costs**: annual investment costs, annual interest rate on investment.
2. **Fixed operating costs**: (service and maintenance, insurance).
3. **Variable operating costs**: (raw material, personal, auxiliary materials, water, waste water treatment and energy).

*Table 21: Cost and revenue assumptions in the economic assessment*

| **Cost item** | **Category** | **Value** |
|---|---|---|
| Investement costs (IC) | Capital costs | 180 – 290 Mio. € |
| Depreciation time | Capital costs | 15 years |
| Interest rate | Capital costs | 5% |
| Service & Maintencance | Fixed operating costs | 3% of IC |
| Insurance | Fixed operating costs | 1% of IC |
| Personnel costs | Variable operating costs | 45000 €/person and year |
| Persons | Variable operating costs | 40 |
| Biomass costs: Straw (90% drymatter) | Variable operating costs | 80 €/t |
| Biomass costs: Woodchips (45% drymatter) | Variable operating costs | 40 €/t |
| Electricity price | Variable operating costs | 80 €/MWh |
| **Revenue item** | | **Value** |
| Electricity | | 50 €/MWh |
| Distric heat | | 20 €/MWh |
| Pellets | | 100 €/t |
| C5 Molasses | | 70 €/t |
| Biomethane | | 30 €/MWh |

Annual investment costs are calculated with an interest rate of 5% and a depreciation time of 15 years. Annual revenues are obtained from the sale of by-products gained in the respective production concept. The cost of bioethanol is calculated as the difference between annual costs and annual revenues and is expressed on volume base (€ per L) and energy base (€ per L gasoline equivalent). Table 21 lists the most important assumptions in the economic assessment. More details about economic assessment method and results can be found in ***Paper V*** and particularly in the final report of the research project [Könighofer *et al.* , 2012].

# II. RESULTS

# PAPER I PRODUCTION CONCEPTS[83]

Kravanja P. and Friedl A. (2010)

Evaluation of ethanol from lignocellulosic biomass – Process scenarios for Austria.

**Chemical Engineering Transaction** 21:1141-1146

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[83] *In this paper the term **process scenarios** is used. Throughout this the term **production concepts** is used instead.*

CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
Copyright © 2010, AIDIC Servizi S.r.l., ISBN 978-88-95608-05-1 ISSN 1974-9791
DOI: 10.3303/CET1021191

# Evaluation of Ethanol from Lignocellulosic Biomass – Process Scenarios for Austria

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In bio-ethanol production lignocellulosic materials such as wood or straw constitute an attractive alternative to starchy feedstock for several reasons. The goal of this paper is to present an approach to determine the most interesting process scenarios for production of lignocellulosic ethanol in Austria. A brief review of the conversion technologies available is given. A selection of relevant conversion processes for Austria is presented. Process modeling as a tool for process analysis is introduced.

## 1. Introduction

In the EU the target for renewable energy in transport has been defined to be 10% at 2020 (European Union, 2009). For several reasons bio-ethanol produced from lignocellulosic materials is an adequate strategy that can contribute to reach this target. First, these materials are available abundantly and consequently affect production economics positively. Second, using parts of the raw material to cover the processes' internal energy demand renders the process ecologically friendly. As a result the greenhouse gas mitigation potential is promising (Eisentraut, 2010; Wang et al., 2007). Moreover, usage of additional acreage can be avoided if residual materials from food production or forest industry are employed.

The technological challenges for ethanol from lignocellulosic biomass are inherent to the feedstock. Structural carbohydrates like cellulose and hemicelluloses are much more recalcitrant to degradation than carbohydrates used for energy storage of the plant. To overcome this recalcitrance of the feedstock sophisticated equipment is necessary which results in a high capital cost of the conversion plant. This high capital cost can outweigh the economical benefits of the cheap feedstock.

## 2. Technology Options

### 2.1 Feedstock

There is a wide range of lignocellulosic feedstock that can be converted to ethanol. In Austria however, the most abundant lignocellulosic raw materials are wood and straw. The major components of any lignocellulosic biomass are the polysaccharides cellulose and hemicellulose and the phenolic polymer lignin. In a biological process polysaccharides which account for up to two thirds of the biomass can be fermented to

Please cite this article as: Kravanja P. and Friedl A., (2010), Evaluation of ethanol from lignocellulosic biomass – Process scenarios for Austria, Chemical Engineering Transactions, 21, 1141-1146 DOI: 10.3303/CET1021191

ethanol whereas lignin cannot be used to produce ethanol but serves as a solid fuel for the process.

### 2.2 Enzymatic Conversion Process

To obtain fermentable sugars from lignocellulosic biomass hemicellulose and cellulose have to be hydrolyzed, which can be achieved via two strategies: acid hydrolysis and enzymatic hydrolysis (Hamelinck et al., 2005). Nowadays there is an agreement, that the enzymatic approach is the most promising technology (Hahn-Hägerdal et al., 2006; Wooley et al., 1999), mainly due to expectable improvements in enzyme technology and the high cost of stainless steel equipment and recovery or neutralization systems necessary in acid processes.

#### *2.2.1 Pretreatment of biomass to improve enzymatic digestibility*

For an efficient use of enzymes the cellulose fibers have to be rendered accessible for enzymatic attack which is achieved by a pretreatment step. There is broad range of pretreatment technologies available, each of which differing in process characteristics and mode of action. The most important technologies are physico-chemical methods like steam pretreatment with addition of acid, like $SO_2$, $H_2SO_4$ or organic acids, dilute acid pretreatment, which is very similar to steam pretreatment, organosolv pretreatments using organic solvents like ethanol or and alkali treatments using lime or ammonia (Galbe and Zacchi, 2007, Mosier et al., 2005). Depending on the pretreatment method and the microorganisms used for ethanol production detoxification can be necessary. In steam pretreatment and dilute acid hydrolysis which are the technologies applied most often hemicellulose is solubilized whereas lignin and cellulose are essentially left intact.

#### *2.2.2 Enzyme production and enzymatic hydrolysis*

After pretreatment the cellulose can be degraded to yield glucose monomers. This is achieved by an cellulase enzyme mixture. Cellulases are extracellular enzymes produced in submerged fermentation under aerobic conditions by specialized microorganisms like *T.reesei* or *A. Niger* (Lynd et al., 2002). At present enzymes are produced in dedicated enzyme production plants, however, economic considerations make on-site production of cellulose enzymes a viable option. In this case part of the pretreated material can serve as a substrate (Szengyel et al., 2000). Enzymes are partly bound to the mycelium and consequently it can be advantageous not to separate the extracellular enzymes from the broth but to add the whole slurry to the hydrolysis step (Kovács et al., 2009; Merino and Cherry, 2007).

In enzymatic hydrolysis a high cellulose conversion at low enzyme loadings, short residence times and a high content of water insoluble solids (WIS) is desired. The high WIS-content is essential since it results in a high concentration of sugars and ethanol which is crucial to reduce the energy demand of distillation.

#### *2.2.3 Ethanol fermentation and biocatalyst propagation*

In the fermentation step the sugars liberated by enzymatic hydrolysis and pretreatment are converted to ethanol by microorganisms. In well established ethanol processes converting starch- or sugar based raw materials *S.cerevisiae* has been the industrial standard. However, its lacking capability to ferment C5-sugars is a major drawback when dealing with lignocellulosic hydrolysates. A possible remedy is the use of recombinant or native C5-sugar-fermenting organisms like *rS. Cerevisiae* or *E.coli, P.stipis and Z.mobilis* (Hahn-Hägerdal et al., 2006; Aden et al., 2002).

Prior to its use in the fermentation step the microorganism has to be cultivated in an aerobic propagation step. To adapt the microorganism to inhibitors present in the hydrolysate, propagation on part of the pretreated material is beneficial (Rudolf et al., 2005; Aden et al., 2002).

Ethanol fermentation can be performed either as a separate step after enzymatic hydrolysis (Separate Hydrolysis and Fermentation, SHF) or simultaneously with hydrolysis (Simultaneous Saccharification and Fermentation, SSF). If SSF is employed end product inhibition in the hydrolysis step can be avoided and capital cost can be reduced. However, with SSF recycling of the microorganisms is not an option and neither of the two steps can be performed at its optimal conditions (Olofsson et al., 2008). An even higher degree of process integration is achieved with Consolidated Bioprocessing (CBP), where enzyme production, cellulose breakdown and alcohol fermentation are performed in one reactor by the same microorganism (Lynd et al., 2002; Lynd et al., 2005).

### *2.2.4 Ethanol recovery, stillage treatment and energy production*

In conventional ethanol processes multicolumn distillation and pressure swing adsorption (PSA) are standard technologies to obtain fuel grade ethanol. Also with lignocellulosic feedstock these technologies are the first choice for ethanol recovery (Aden et al., 2002; Sassner et al., 2008) even though there exists a whole range of attractive alternative separation technologies like membrane-, stripping- and extraction-technologies that might be advantageous for the more dilute fermentation broths obtained from lignocellulosic hydrolysates (Vane, 2008).

To render the whole process energy efficient the stillage has to be used to supply process energy. For that purpose the insoluble solids are typically separated from the liquids dried and burnt. Solids exceeding the amount needed to cover the processes energy demand can be sold as a solid fuel. The liquid fraction can be evaporated; vapors are condensed and recycled to the process. The liquid effluent (syrup) after evaporation can be burnt together with the solids (Aden et al., 2002; Sassner et al., 2008) or used as an animal feed (Larsen et al., 2008). An alternative to evaporation is anaerobic digestion of the liquid fraction (Wingren et al., 2008). The biogas yielded can be used for generation of heat or electricity production in an engine.

## 3. Process Scenarios for Austria

In Austria the most relevant raw materials for production of lignocellulosic ethanol are straw, hardwood and softwood. Raw material potentials and feedstock logistics suggest the annual ethanol capacity of the plants to be in the range of 50 000 to 100 000 t/a for hardwood and straw and 50 000 to 200 000 t/a for softwood.

In order to assess the most promising process scenarios for Austria the following eligibility criteria were applied: economic aspects, technology proven in pilot-scale, energy self-sufficiency and legal situation in Austria. This led to the conclusion that the main distinctive feature for Austrian scenarios is stillage treatment. As a result the process scenarios are identical regarding the upstream process steps size reduction, steam pretreatment, enzyme production, yeast propagation and SSF as well as the

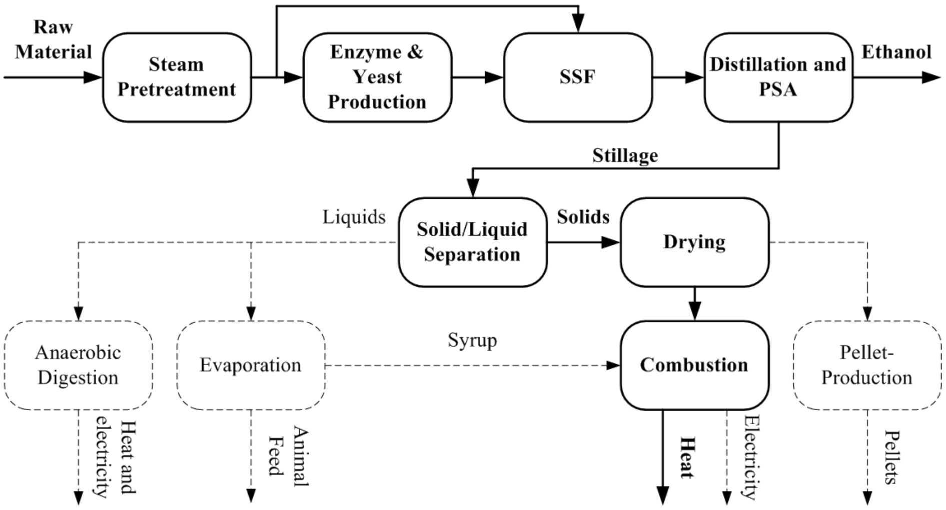

*Figure 1 Summary of process scenarios differing in stillage treatment. Bold text and a solid line symbolize process steps and streams that are applied in all the scenarios. Dashed lines symbolize process steps and streams that are only applied in selected scenarios.*

downstream steps distillation and pressure swing adsorption (PSA). As far as stillage treatment is concerned all the concepts introduced in section 2.2.4 are considered. Figure 1 shows a scheme of the scenarios differing in stillage treatment. Due to legal restraints in Austria fermentation of C5-sugars is not considered except for one case, which accounts for possible future changes in legislation. Table 1 summarizes the process scenarios.

*Table 1 Summary of process scenarios.*

| Raw Material | Fermentation | Stillage Treatement |
|---|---|---|
| Softwood | C6 sugars | Evaporation, combustion of solids and syrup, heat and A) pellets or B) electricity production |
| Hardwood | C6 sugars | Evaporation, Combustion of solids and syrup, heat and A) pellets or B) electricity production |
| Straw | C6 sugars | Evaporation, combustion of solids and syrup, heat and A) pellets or B) electricity production |
| Straw | C6 sugars | Evaporation, combustion of solids, animal feed from syrup, heat production |
| Straw | C6 sugars | Anaerobic digestion of liquids, combustion of solids, heat and electricity production |
| Straw | C6 & C5 sugars | Evaporation, combustion of solids and syrup, heat and A) pellets or B) electricity production |

## 4. Process Modelling with IPSEpro

Analysis of the process scenarios is performed via process simulation. Thereto the commercial steady state flowsheet simulation package IPSEpro is applied. The software was developed for the simulation of power plants. Consequently the standard advanced power plant library (APP_lib) contains accurate property data and basic equipment for power plant computations. Due to the flexible structure of IPSEpro's model development kit (MDK) the APP_lib can be rather easily extended by the materials and unit-operations present in biotechnological production processes of liquid and gaseous fuels from renewable materials, as shown in a prior study (Schausberger et al., 2009). Within IPSEpro's process simulation environment (PSE) graphical representations of the unit-operations are used for flowsheeting. Thanks to IPSEpro's equation oriented solving approach input and output information can be exchanged arbitrarily and complex flowsheets including recycle streams converge quickly. Consequently energy integration of the process using pinch technology can be realized easily.

For upcoming simulations of the scenarios described above, the model library was extended by materials and unit operations present in a lignocellulosic ethanol process. Future work is dedicated to flowsheet simulation of the process scenarios yielding detailed description of energy and material flows.

## 5. Conclusions

In this paper a brief review on the production of ethanol from lignocellulosic feedstock is given, the most relevant process scenarios for Austria are presented and an approach for modeling the conversion processes is introduced. The results obtained from process modeling can serve as a basis for techno-economic assessment, life cycle analysis, as well as energy- and exergy analysis of the process scenarios. The analysis' results should indicate the most viable process configurations of a demo-plant in Austria.

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# PAPER II HEAT INTEGRATION

Kravanja P., Modaressi A. and Friedl A. (2013)

Heat integration of biochemical ethanol production from straw - A case study.

**Applied Energy** 102:32-43

Applied Energy 102 (2013) 32–43

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

# Heat integration of biochemical ethanol production from straw – A case study

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## HIGHLIGHTS

- ▶ We perform heat integration of ethanol production from straw.
- ▶ In pinch analysis distillation and evaporation design are examined in detail.
- ▶ Via pinch analysis the design is improved and the utility targets reduced by 15%.
- ▶ For the improved design an efficient heat exchanger network was obtained.
- ▶ For this network 50% of residual materials suffice to provide process heat.

## ARTICLE INFO

*Article history:*
Received 3 February 2012
Received in revised form 10 August 2012
Accepted 10 August 2012
Available online 18 September 2012

*Keywords:*
Bioethanol
Lignocellulose
Straw
Heat integration
Pinch analysis
Heat exchanger network

## ABSTRACT

Ethanol produced from lignocellulosic biomass is a desired, renewable fuel that can help to reduce our dependence on oil. In order to achieve the commercial deployment of this fuel good economic and environmental performance are mandatory. Both these targets are tackled by the efficient use of process heat. This work deals with the heat integration of the biochemical production of ethanol from straw. Process simulation and pinch analysis are applied to investigate a base case design of the production process. The energy intensive unit operations distillation and evaporation are in the focus of this pinch analysis. Pressure and heat load modifications of these sections are applied to improve the process design. For this improved process design a heat exchanger network is synthesized. Energy stream and pinch analysis revealed that process residues easily suffice to provide the investigated process with heat. The design modifications of the distillation and evaporation sections lead to increased heat integration. Consequently, a 15% reduction of the utility targets compared to the base case is obtained in the improved design. The heat exchanger network for the improved design is simple, yet the increase in utility consumption compared to the utility targets is quite modest. As a result, in the network only 51% of waste biomass suffice to provide the process with heat. The exceeding biomass can be used for the recovery of energy or material by-products, which highlights the need for efficient polygeneration concepts.

## 1. Introduction

It is widely accepted that bioethanol from lignocellulosic feedstock should play an important role in the energy system of the future. This consensus, based on several appealing features of the fuel and the technology, is expressed in policies in both, the EU and the US [1–3]. Bioethanol is a renewable fuel that reduces our dependence on oil, has very good combustion properties and can be applied to the existing car fleet when blended at low concentrations [4]. The greenhouse gas mitigation potential of lignocellulosic ethanol is high compared to both, fossil fuels and bioethanol from starchy crops [5,6]. Ultimately, the food vs. fuel debate can be avoided, when lignocellulosic waste materials are used for the production of bioethanol.

At present, the technology is limited to the demonstration scale. For commercial production lignocellulosic ethanol has to be economically feasible and environmentally friendly. A common strategy to achieve this goal is to provide process heat by burning the lignin-rich process residues and thereby avoid the use of external, fossil fuels [7–10]. Another way to reach this goal is to increase the process efficiency by means of process integration. For this task, pinch technology can be employed in different ways.

A first strategy is to use pinch technology to improve the core process design. Using this approach, Fujimoto et al. [11] found that a heat pump can significantly improve the process efficiency of a lignocellulosic ethanol production process based on concentrated acid hydrolysis. Another strategy to increase process efficiency by means of pinch technology is to optimize the CHP or polygeneration system associated with utility allocation. Zhang et al. [12] used this approach to investigate different polygeneration options for a lignocellulosic ethanol process employing two-stage dilute acid

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http://dx.doi.org/10.1016/j.apenergy.2012.08.014

hydrolysis and significantly improved process efficiency. Ultimately, Morandin et al. [13] combined the two strategies and used pinch analysis for parameter optimization of the core process as well as for validation of different CHP systems. For a process producing ethanol and sugar from sugarcane parameter optimization resulted in a heat demand reduction of one third. In addition, the net power output of the associated CHP system was maximized.

### 1.1. Aim and scope of the paper

In this work we aim to thermally integrate the biochemical production process of ethanol from straw using pinch analysis and heat exchanger network synthesis. The process under consideration is made up of the unit operations steam pretreatment, on-site enzyme and yeast production and simultaneous saccharification and co-fermentation (SSCF) of C5 and C6 sugars to convert straw to ethanol. The ethanol product is recovered and purified by means of distillation and pressure swing adsorption. The stillage from distillation is treated using solid–liquid separation, multi-stage evaporation and superheated steam drying of solid residues.

We start our work with a base case flowsheet model of the process and aim to (i) find options to improve this base case design and (ii) create a fully integrated flowhsheet model of the improved process design. Thereto we apply pinch analysis and heat exchanger network synthesis. As a result of this procedure, a heat exchanger network and the utility requirement of the fully integrated production process are obtained. The mass balances for the process can be closed and general conclusions about the technology can be drawn. Future work will be dedicated to further process analysis (e.g. exergy analysis, economic evaluation or life cycle analysis).

## 2. Methodology

The methodology followed in this work is schematized in Fig. 1. First, a flowsheet model of the base case design for the production process is developed. From this flowsheet model, data is extracted for pinch analysis. The pinch analysis focuses on the energy intensive downstream unit operations distillation and evaporation. Following a well-established procedure [14], these unit operations are analyzed separately from the background process. The findings from this pinch analysis allow us to derive modifications of the process design. These modifications concern the above mentioned unit operations distillation and evaporation and include a change of (i) the number of stages in these unit operations, (ii) the temperature level of the stages and (iii) the heat load of the stages. These design modifications aim at increased heat integration and are implemented to create a flowsheet model of the thus obtained improved process design. Again, data extraction and pinch analysis are performed for the improved design in order to assess the proposed design modifications. Thereto the utility targets of the base case design and the improved design are compared. To complete this heat integration study, a heat exchanger network is developed for the improved process design.

### 2.1. Flowsheet simulations

Steady state flowsheet simulations are performed using the equation oriented software “IPSEpro”. The software was developed for simulation of power plants [15]. Hence, detailed property data and unit operations are available for power plant computations only. For simulation of the process considered in this work a suitable model library was developed [16]. Due to “IPSEpro’s” equation oriented solving approach input and output information can be exchanged arbitrarily and complex flowsheets including recycle streams converge quickly. For heat integration, thermal process data obtained from simulations with IPSEpro is extracted, exported to Microsoft Excel and from there imported to the pinch analysis and heat exchanger network software described in Sections 2.2 and 2.3.

### 2.2. Pinch analysis

Pinch analysis is a powerful methodology to determine options for process heat recovery. In this work it is carried out using the pinch analysis module of the software “TVTHENS”. “TVTHENS” was developed at the Vienna University of Technology using the computational software program “Mathematica”. After data extraction (see Section 3.1) and energy stream investigation according to [14,17], thermal data of the cold streams needing heating and hot streams needing cooling are entered into “TVTHENS” via Microsoft Excel. Based on these data and a specified minimum temperature difference $\Delta T_{\min}$ of 10 °C that is applied in pinch analysis throughout this work, composite curves and grand composite curves representing the minimum heating and cooling demands are constructed by a graphical approach introduced by Salama [18]. For streams without phase change constant heat capacities are assumed. To deal with isothermal streams involved in the process, it is assumed that these streams have 1 °C temperature difference during phase

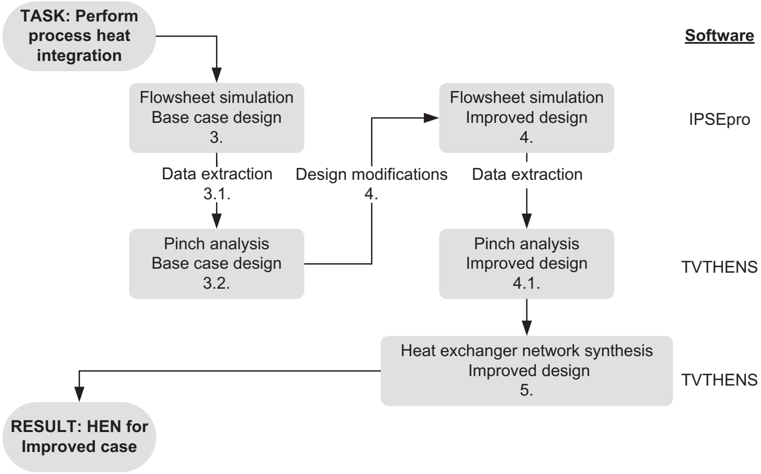

**Fig. 1.** Methodological workflow and simulation tools used. The numbers indicate the respective sections of the text. HEN: Heat exchanger network. Numerals stand for the respective sections of the text.

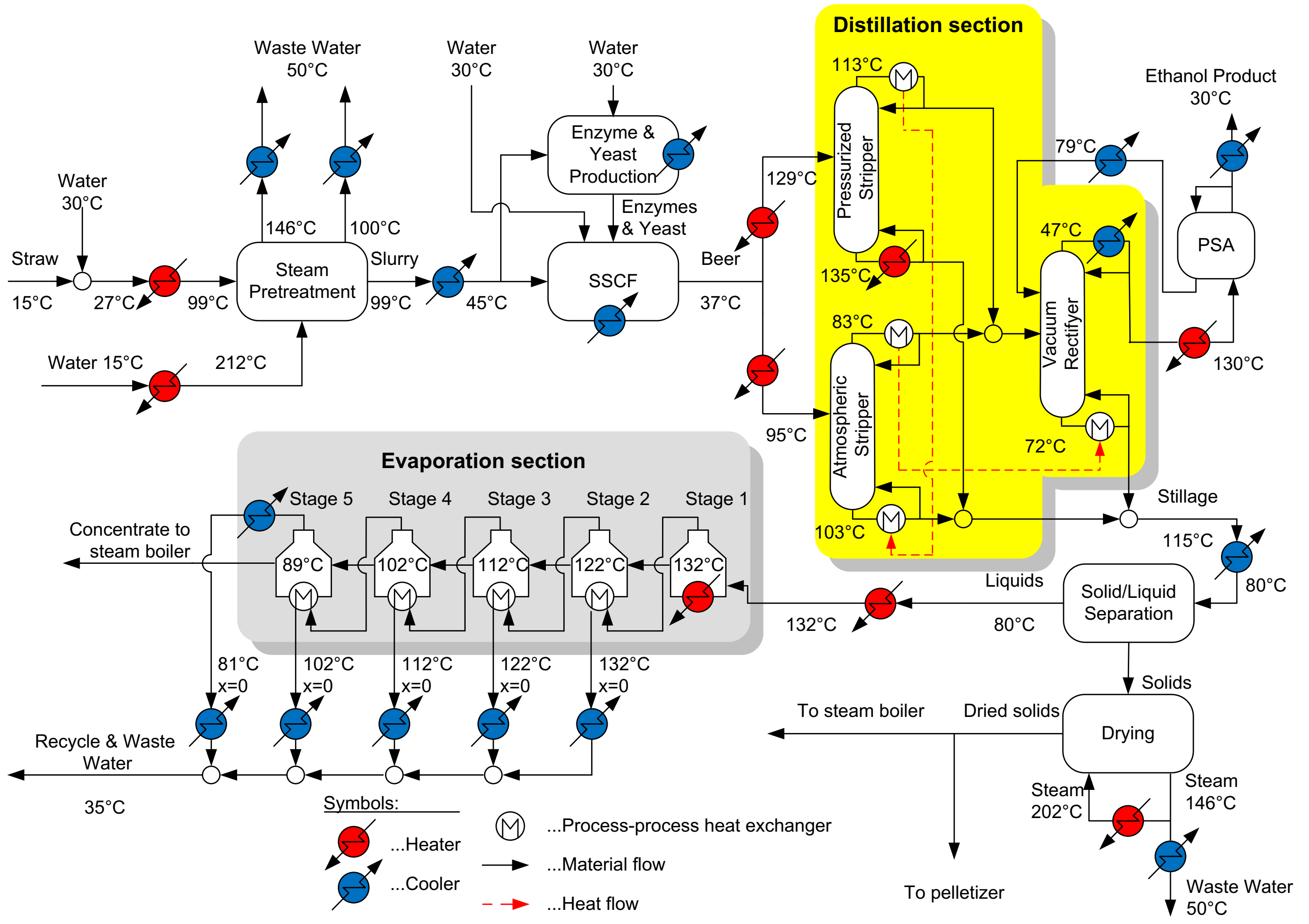

**Fig. 2.** Scheme of the base case design including stand-alone optimized distillation and evaporation section. SSCF: simultaneous saccharification and co-fermentation. PSA: pressure swing adsorption. For simplicity reasons yeast and enzyme production are unified in one block.

change. Fore more details about the pinch analysis principles applied see [14,17].

### 2.3. Heat exchanger network synthesis

Heat exchanger network synthesis was performed with the respective program module of “TVTHENS”. The program module for heat exchanger network design considers process streams that undergo both sensible and latent heat changes (e.g. streams in the multi stage evaporation) and utilizes an extended mixed integer linear programming (MILP) model proposed by Ponce-Ortega [19]. This model is based on the superstructure formulated by Yee and Grossmann [20] in which the total annual cost including utility and heat exchanger costs is minimized. The “Mathematica” optimization package makes it possible to reduce computational time for industrial scale problems. The network synthesis was performed with for a $\Delta T_{\min}$ of 10 °C. In order to keep the network simple, stream splitting was excluded in the network synthesis.

## 3. Base case design

Fig. 2 shows the base case design of the process. This design builds on the work at Lund University, Sweden [9,21,22] and employs efficiently integrated stand-alone solutions for the thermal separation units distillation and evaporation. The mass and energy balances are calculated for an ethanol production capacity of 100,000 t/y and operating time of 8000 h/y.

Shredded straw (90 dry matter, DM) is wetted to reach a moisture content of 65% and preheated close to the boiling temperature of water. The moistened and preheated straw is impregnated with $SO_2$ and steam pretreated at 190 °C. Heat losses are assumed to amount to 10% of total heat transferred. As suggested by Wingren [23], the flashing after steam pretreatment is performed in two steps, first at medium pressure (MP) at approx. 4.3 bar and then at atmospheric pressure (AP). Flashing yields saturated secondary steam at the respective levels. After condensation and cooling to 50 °C the condensates from steam pretreatment have to be disposed of.

The hot slurry after steam pretreatment is neutralized using $NH_4(OH)$, cooled to 45 °C and split into three streams. The major part of the slurry is directly fed to SSCF where both, C6 and C5 sugars are fermented to ethanol. Minor parts of the slurry are used for enzyme production (EP) and yeast propagation (YP). The mass flows of the streams to EP and YP are a result of the conversions in the bio-reactors on the one hand and enzyme and yeast requirements in SSCF on the other hand. SSCF is performed at 37 °C, whereas yeast propagation and enzyme production are performed at 30 °C. The slurry however, is only cooled to 45 °C, since dilution with colder water is necessary to decrease the solid content and the concentration of inhibitors formed in the pretreatment. Moreover, the bioreactors require cooling to remove heat released from the respective reactions.

After conversion of sugars to ethanol in SSCF the beer stream contains approx. 6 w/w% ethanol. This stream is split into two streams, preheated and fed to the thermally integrated three column distillation section. As suggested by Wingren, this section consists two parallel stripper columns, one operated at elevated pressure and one under atmospheric conditions, and a vacuum rectifier column [21]. The pressurized stripper requires heat at MP level. Condenser heat from the pressurized stripper is used to heat the atmospheric stripper whose condenser heat in turn is used to heat the vacuum rectifier. The split ratio of the feed stream and the distillation operating conditions are chosen in a way, that no external heat is necessary to heat atmospheric stripper or the rectifier. To compensate for heat losses in the columns, the reboiler heat duties are approx. 5% lower than the condenser heat duties by which they are supplied. To enable heat exchange between hot and cold streams a $\Delta T$ of 10 °C is assumed. Condensation heat at the head of the rectifier has to be removed at 47 °C. The 92 w/w% ethanol head product is compressed, superheated to 130 °C and sent to a pressure swing adsorption (PSA) unit. In PSA ethanol is purified to 99.5 w/w%. 25% of the purified ethanol is used to purge the loaded bed. The regenerate obtained from purging is condensed and returned to the rectifier. Purified ethanol is condensed and cooled to 30 °C.

The stillage stream from distillation contains all the solids, water and by-products of prior conversion steps. This stream is cooled to 80 °C and sent to a filter press where liquids and soluble solids are separated from insoluble solids. A dry matter content of 45% of the solid fraction and 99% recovery of insoluble solids are assumed. The liquid fraction containing most of the soluble solids is preheated for evaporation and concentrated to 65% DM in a 5 stage co-current evaporation train. The feed stage is operated at a pressure requiring MP steam, whereas the last stage is operated at 0.5 bar. In each stage heat losses are assumed to amount to 10%. Operating pressures in the stages 1–5 are set to 2.9, 2.1, 1.5, 1 and 0.5 bar resulting in 10 °C $\Delta T$ between the stages (see Fig. 2). Complete condensation ($x = 0$) is assumed, when the vapors from stages 1–4 are used for heat exchange with subsequent stages. The boiling point elevation was considered using an empiric expression [24]. The condensed vapors from the first four stages are cooled to 35 °C. Vapor from the last stage is condensed and cooled to 35 °C. A part of the condensate can be recycled to the process [24], the rest is disposed of. The concentrate from evaporation is sent to the steam boiler.

For drying of insoluble solids a superheated steam dryer working at MP level can be employed [21]. During the drying the water content is reduced to 10%. The steam serving as drying medium is produced from water evaporated from the solids. In a closed loop the steam is superheated indirectly [25]. In addition excess MP steam that can be used elsewhere in the process is produced. After condensation and cooling to 50 °C this stream has to be disposed of. Again, heat losses are assumed to amount to 10%. As indicated in Fig. 2, hot utilities are provided by feeding parts of the dried solids together with the concentrate from evaporation to a steam boiler. Excess solids can be pelletized and sold.

A flowsheet model of this process design was developed in “IPSEpro”. The overall process ethanol yield is 70.4%, based on C6 and C5 sugars available in the raw material. 446,000 t of straw (252 MW) are thus required annually to produce 100,000 t of ethanol (93 MW). Moreover, some 150,000 t of dried solids (84 MW) and 112,000 t of evaporation concentrate (56 MW) are obtained. The corresponding energy flows in parentheses are based on the lower heating value (LHV). The lower heating values for biomass streams were calculated using the PLS model of Friedl et al. [26].

### 3.1. Data extraction for pinch analysis

All hot and cold process streams extracted from a flowsheet model of the base case design are listed in Table 1. To cover the entire process utility demand the cooling of bio-reactors operated in batch-mode is also included. To check and improve their design the energy intensive distillation and evaporation sections are singled out from the background process [14]. As described in Section 3 and shown in Fig. 2, the thermal separation units distillation and evaporation are designed in a way that external heat is only required at the first stage operated at the highest pressure and external cooling is only required at the last operated at the lowest pressure. Consequently, for the base case all other hot or cold streams of the distillation and evaporation sections are either not listed in Table 1 (condenser of the press. stripper, vapors evap. stage 1 and 2, heat evap. stages 2, 3 and 5) or the respective data is not included (n.i.) in Table 1. As indicated in Fig. 2, heating the feed to distillation and evaporation as well as cooling of the stillage and condensed vapors are covered in the background process [14]. Hot utility generation in the steam boiler is not included. However, steam for pretreatment is included, because this stream is a reactant in the pretreatment step and not a true utility [17].

By summing up all the heat loads of all cold and hot streams, the maximum hot and cold utility requirement $Q_{HU,max}$ and $Q_{CU,max}$ of the base case are obtained. They amount to 113.3 and 100.2 MW, whereof 71.1 and 71.0 MW are required for heating and cooling of the background process. The remaining 42.3 and 29.2 MW are needed to heat and cool the distillation and evaporation sections. Almost 40% of hot utility are thus required to heat these energy intensive unit operations even though energy efficient multi-stage solutions have been implemented. This finding clearly illustrates why these sections should be in the focus of the following pinch analysis.

### 3.2. Pinch analysis of the base case

To perform pinch analysis of the base case design, the extracted data was entered to “TVTHENS” (see Section 2.2). The resulting grand composite curves (GCCs) are shown in Fig. 3.

Fig. 3a shows the GCC of the background process separated from the distillation and evaporation sections. These sections are represented as boxes [14]. The hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ of the background process both account for approx. 30 MW. Hence, 41 MW of heat can potentially be recovered in the background process. The pinch point of the background process is located at a shifted temperature $T^*$ of 141 °C, the condensation temperature of MP steam obtained from steam pretreatment and drying. This location of the pinch point indicates that the background process cannot fully absorb the heat from steam pretreatment and drying. As shown in Fig. 3a, some 11 MW of excess heat are obtained in that way.

The distillation and evaporation sections are well placed below the pinch of the background process [15]. However, the 11 MW of excess heat at MP level do not suffice to provide heat for both thermal separation units. Hence, integrating the distillation and evaporation sections could potentially lead to further energy savings.

Fig. 3b shows the overall grand composite curve, representing the entire base case process including distillation and evaporation. The overall process utility targets $Q_{HU,min}$ and $Q_{CU,min}$ thus obtained amount to 61 MW and 48 MW. By subtracting the targets from the 113 MW and 100 MW representing the maximum hot and cold utility requirement $Q_{HU,max}$ and $Q_{CU,max}$ of the base case one finds a heat recovery of 52 MW corresponding to a 46% and 52% reduction of hot and cold utility consumption. Comparing the 52 MW to the 41 MW of heat recovery in the background process reveals that the integration of the distillation and evaporation sections with the background process leads to an increase in heat integration by 11 MW. This integration is due to utilization of excess MP steam from the background process, which can be used to heat the distillation or evaporation. This option for heat recovery is reflected in the very sharp pocket at a $T^*$ of 141 °C. It is important to note that

**Table 1**
Hot and cold streams in the background process, distillation section and evaporation section. Streams differing in the base case and improved case are shown in bold characters. For these streams data for the base case are indicated before the backslash whereas data for the improved case are indicated after the backslash.

| Stream description | Alias | $T_{\mathrm{in}}$ (°C) | $T_{\mathrm{out}}$ (°C) | $T_{\mathrm{Phasechange}}$ (°C) | $Q_{\mathrm{Phasechange}}$ (MW) | $Q_{\mathrm{total}}$ (MW) |
|---|---|---|---|---|---|---|
| *Background process cold streams* | | | | | | |
| Straw to SP | C01 | 27 | 99 | | | 9.2 |
| Steam for SP | C02 | 15 | 212 | 211 | 13.8 | 20.0 |
| **Beer to atm. stripper** | **C03** | **37** | **95** | | | **6.4/13.6** |
| **Beet to press. stripper** | **C03a** | **37/–** | **129/–** | | | **11.5/–** |
| Vapors to PSA | C04 | 105 | 130 | | | 0.2 |
| Feed to evap. section | C05 | 80 | 133 | | | 10.3 |
| Superheat drying steam | C06 | 150 | 202 | | | 13.5 |
| *Background process hot streams* | | | | | | |
| MP steam from SP + dryer | H01 | 146 | 50 | 146 | 19.2 | 23.0 |
| AP steam from SP | H02 | 100 | 50 | 100 | 6.9 | 7.6 |
| Slurry from SP | H03 | 99 | 45 | | | 7.2 |
| Yeast production | H04 | 30 | 29 | | | 1.2 |
| Enzyme production | H05 | 30 | 29 | | | 0.7 |
| SSCF | H06 | 37 | 36 | | | 3.4 |
| Ethanol product | H07 | 130 | 30 | 79 | 3.0 | 3.8 |
| Regenerate from PSA | H08 | 137 | 78 | 79 | 1.8 | 2.0 |
| **Stillage** | **H09** | **116/101** | **80** | | | **8.0/4.6** |
| **Condensate evap. stage 1** | **H10** | **132/134** | **35** | | | **4.0/5.5** |
| **Condensate evap. stage 2** | **H11** | **122/124** | **35** | | | **3.4/4.6** |
| **Condensate evap. stage 3** | **H12** | **112/113** | **35** | | | **2.9/3.7** |
| **Condensate evap. stage 4** | **H13** | **102/66** | **35** | | | **2.3/0.9** |
| **Condensate evap. stage 5** | **H14** | **81/–** | **35/–** | | | **1.5/–** |
| *Distillation section cold streams* | | | | | | |
| **Reboiler press. stripper** | **CD0** | **134/–** | **135/–** | **134/–** | **18.7/–** | **18.7/–** |
| **Reboiler atm. stripper** | **CD1** | **n.i./103** | **n.i./104** | **n.i./103** | **n.i./28.6** | **n.i./28.6** |
| **Reboiler vac. rectifyer** | **CD2** | **n.i./72** | **n.i./73** | **n.i./72** | **n.i./28.6** | **n.i./17.3** |
| *Distillation section hot streams* | | | | | | |
| **Condenser press. stripper** | **HD0** | **n.i./ –** | **n.i./ –** | **n.i./ –** | **n.i./ –** | **n.i./ –** |
| **Condenser atm. stripper** | **HD1** | **n.i./84** | **n.i./83** | **n.i./84** | **n.i./26.8** | **n.i./26.8** |
| **Condenser vac. rectifyer** | **HD2** | **48** | **47** | **48** | **11.6/12.1** | **11.6/12.1** |
| *Evaporation section cold streams* | | | | | | |
| **Heat evap. stage 1** | **CE1** | **132/134** | **133/135** | **132/134** | **23.6/32.1** | **23.6/32.1** |
| **Heat evap. stage 4** | **CE4** | **n.i./73** | **n.i./74** | **n.i./73** | **n.i./16.6** | **n.i./16.6** |
| *Evaporation section hot streams* | | | | | | |
| **Vapors evap. stage 3** | **HE3** | **n.i./114** | **n.i./113** | **n.i./114** | **n.i./25.3** | **n.i./25.3** |
| **Vapors evap. stage 4** | **HE4** | **n.i./73** | **n.i./66** | **n.i./73** | **n.i./16.8** | **n.i./16.8** |
| **Vapors evap. stage 5** | **HE5** | **89/–** | **81/–** | **89/–** | **17.6/–** | **17.6/–** |

n.i.: stream not included because it is fully integrated; –: stream does not exist in the improved design, SP: steam pretreatment; pres.: pressurized; atm.: atmospheric; vac.: vacuum; PSA: pressure swing adsorption; MP: medium pressure; AP: atmospheric pressure; SSCF: simultaneous saccharification and co-fermentation; evap.: Evaporation.

the pinch point of overall process has shifted to 95 °C, the condensation temperature of AP steam. This is because in the overall process MP steam is entirely consumed. However, in Fig. 3b, it can be seen that now AP steam obtained from steam pretreatment does not contribute to the heat integration. In an improved process design, this heat should be utilized.

To determine major options for heat recovery in the background process one should keep in mind, that the region above the overall pinch (95 °C) is a heat sink and the region below the overall pinch is a heat source [14]. Hot streams above the overall pinch and cold streams below the overall pinch can thus be fully integrated (see Table 1). The most prominent cold streams below the pinch are (i) the straw before pretreatment (C01), (ii) the water for steam pretreatment (C02), (iii) the beer before distillation (C03 and C03a) and (iv) the feed to evaporation (C05). On the other hand, the most important hot streams above the pinch are (i) the stillage (H09) and (ii) the condensates from evaporation (H10–H13). These hot and cold streams thus provide the greatest potential for heat recovery in the background process.

To sum up, the base case design has significant potential for heat integration and utility reduction. This potential originates from (i) the background process as such and (ii) the excess MP steam from pretreatment and drying that can be used to integrate the distillation and evaporation with the background process. However, the heat integration could be further improved e.g. by integrating the distillation and evaporation sections and shifting some of the heat demand from the MP to the AP level.

## 4. Improved process design

In principle, there are several strategies available to reduce the utility consumption in the prevailing heat recovery problem. Due to the capital-energy trade-off decreasing $\Delta T_{\mathrm{min}}$ or increasing the number of stages in the distillation or evaporation sections are not considered acceptable options. Certainly, the strategy followed in this work relies on pinch based process modifications resulting in an increased integration of the thermal separation units. Thereto pressure modifications that result in temperature shifts of the heat loads are applied. Admittedly, in this context some limitations must be considered.

In the base case design both, distillation and evaporation are placed below the pinch. In principle, energy savings could be obtained by increasing the operating pressure and thereby shifting one of the sections or parts thereof above the pinch. For the evaporation stages and the stripper columns, this is not feasible due to the degradation and fouling of sugars and other organic compounds above 140 °C. Since no easily degradable compounds enter

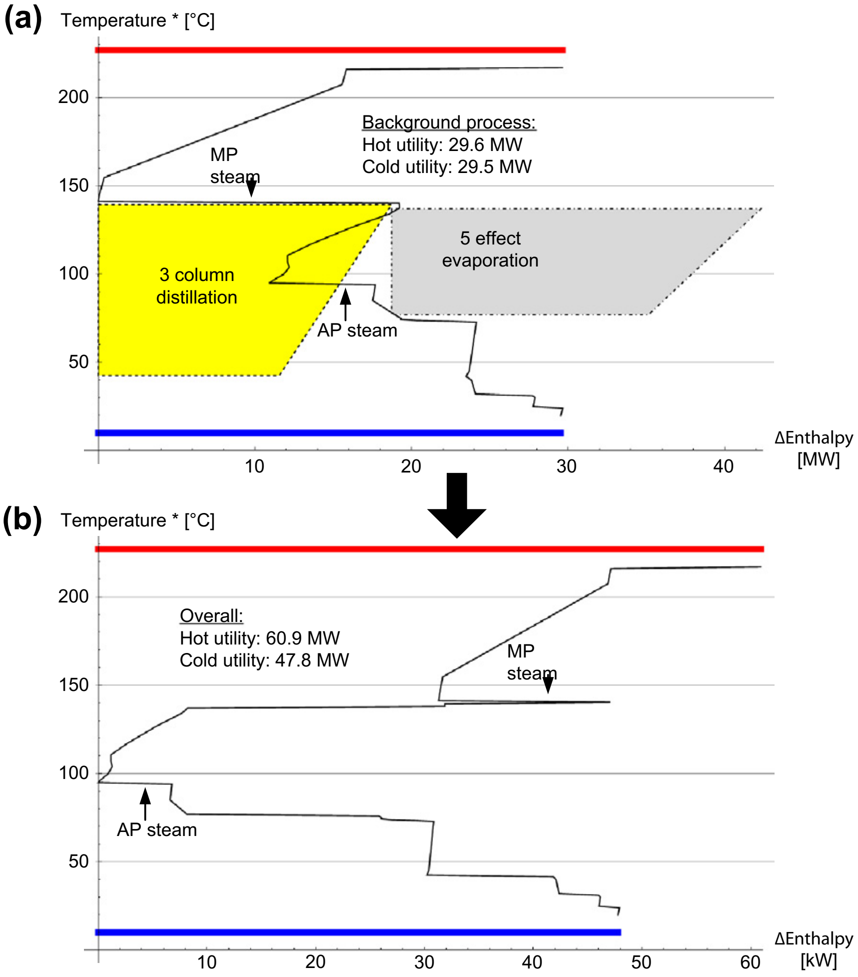

**Fig. 3.** Grand composite curves (GCCs) of base case. (a) GCC of background process. Distillation and evaporation are represented separately as boxes. (b) Overall GCC including the thermal separation units.

the rectification, it could potentially be shifted above the pinch. However, as can be seen in Fig. 3a, the background process could absorb the heat released at the condenser of the distillation only at temperatures above 200 °C. The associated increase of material cost and the requirement for an additional hot utility level makes this option unattractive.

On the other hand, process modifications resulting in very low temperatures and pressures should also be avoided, since vacuum generation is capital intensive and requires a lot of electricity. When very low pressures are applied, a potential heat load reduction thus corresponds to an undesired increase in electricity consumption.

Summing up, the following restrictions were applied in altering the design of the distillation and evaporation sections:

- No increase of stages in evaporation or distillation compared to the base case.
- No reduction of $\Delta T_{min}$.
- No decrease of condensation temperatures/pressures compared to the base case.
- No heating above 135 °C.

Applying these restrictions, design modifications of the thermal separation sections were performed. Following the graphical approach described by Smith [14], heat loads and temperature levels were modified to increase the heat integration. The resulting improved design with integrated distillation and evaporation sections is shown in Fig. 4. Compared to the base case design the pressurized stripper column and one evaporation stage are removed from the design. This reduction of stages is necessary to enable the integration of the distillation and evaporation section under the conditions listed above.

The first stage of the co-current evaporation train still requires MP steam. The heat released by condensation of the vapors from the third evaporation stage is used to supply the reboiler of the atmospheric stripper column, whose condenser duty in turn is used to heat the rectification column and the fourth stage of evaporation, both operated under vacuum.

The improved design was implemented in “IPSEpro”. The stream data extracted from a converged flowsheet simulation of the improved case are in shown in Table 1. Streams differing from the base case are shown in bold characters. Altered data are indicated after the backslashes. As can be seen in Table 1, the modifications of the distillation and evaporation sections also affect the background process. The removal of the pressurized stripper results in reduced heat and cooling duties for preheating the beer and cooling the stillage, whereas the modification of the evaporation section only results in changed cooling requirements of the condensate streams.

### 4.1. Pinch analysis of the improved design

As for the base case, pinch analyses with a $\Delta T_{min}$ of 10 °C were carried out using the stream data from Table 1. The resulting grand composite curves (GCCs) are shown in Fig. 5.

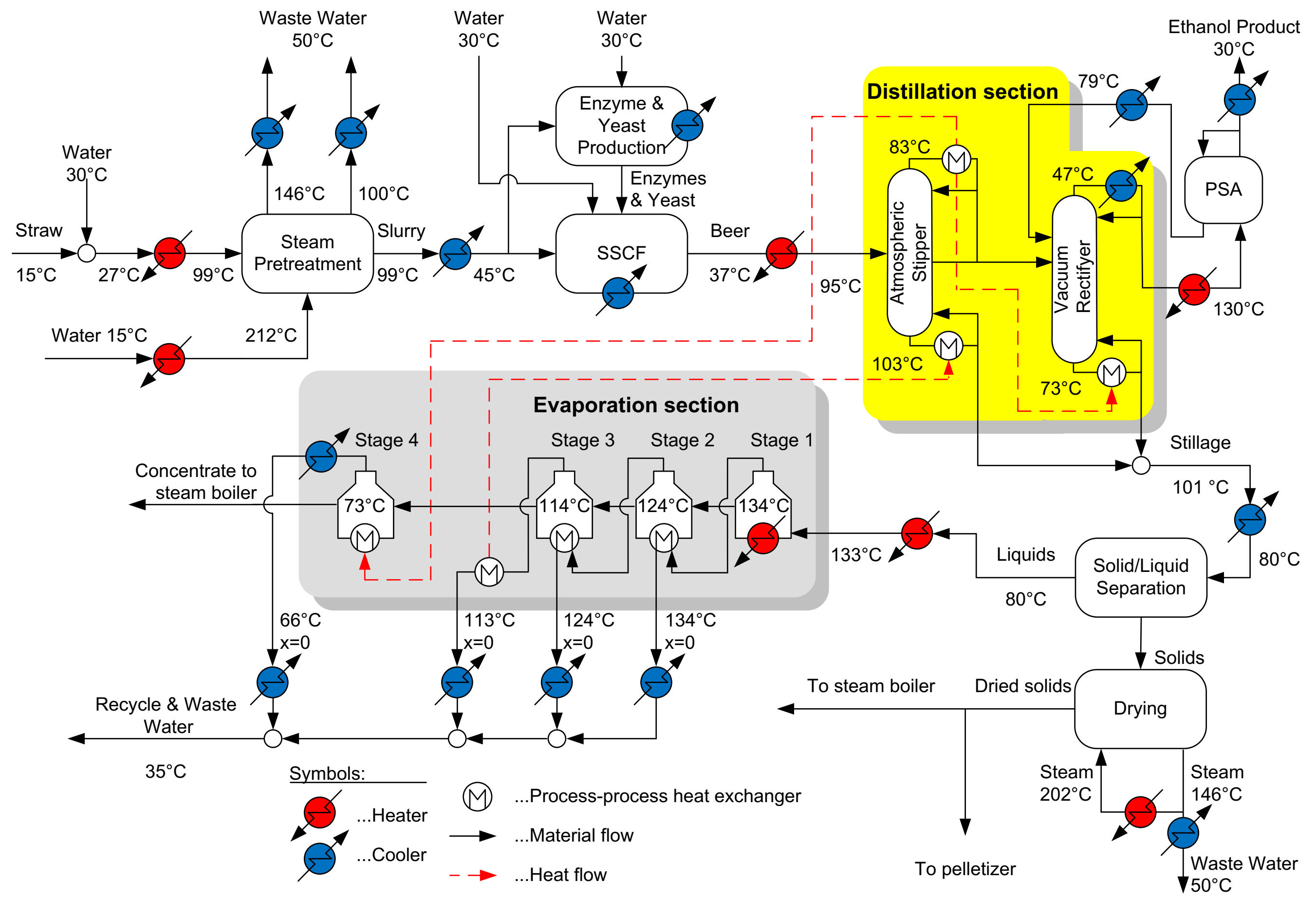

**Fig. 4.** Scheme of the improved design including integrated distillation and evaporation sections. SSCF: simultaneous saccharification and co-fermentation. PSA: pressure swing adsorption.

Corresponding to Fig. 3a, in Fig. 5a the grand composite curve of the background process is shown separately from the distillation and evaporation boxes. In the improved design the hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ of the background process amount to approx. 30 MW and 31 MW. The slightly higher cold utility target for the background process compared to the base case is due to a lower heat demand below the pinch which results in decreased heat integration.

The integration of the distillation and evaporation is clearly visible. Since the distillation was shifted below the first three stages of evaporation, in the improved design MP steam is only required to heat the first evaporation stage and consequently the requirement at MP level is reduced compared to the base case. As can be seen, the heat duty of the evaporation is shifted towards the stages 1–3 whereas the last stage is designed with a smaller heat duty. This shifting of heat loads is beneficial for another reason also: The higher solids loading in the last stage result in a lower heat transfer. Even though the heat duty of the atmospheric stripper column has significantly increased compared to the base case, it can almost entirely be covered by the condensation of vapors from the third evaporation stage. In turn, the rectifier column and the 4th evaporation stage can, to a large extent, be supplied by the condensation heat released at the head of the stripper column.

The increased heat integration is also reflected in Fig. 5b, which shows the overall grand composite curve for the improved design. As a result of the increased integration, the overall hot and cold utility targets $Q_{HU,min}$ and $Q_{CU,min}$ for the improved design are lowered to 52 MW and 40 MW compared to 61 MW and 48 MW for the base case. This is a reduction by 14% and 16% which is attained in spite of the reduction of stages in both distillation and evaporation.

For heat integration between distillation and evaporation a $\Delta T$ only slightly above $\Delta T_{\min}$ was adopted and consequently only rudiments of pockets indicate the respective heat recovery at $T^{*}$ of 110 and 80 °C. One should bear in mind, that pockets of heat recovery are only displayed when $\Delta T_{\min}$ is exceeded. The increased integration between the background process and the thermal separation units is clearly visible by the pocket that is formed between 95 and 80 °C. Here AP steam from steam pretreatment can be used to cover that portion of the heat requirement of the vacuum rectifier and the last evaporation stage that cannot be provided by the condenser of the stripper column.

## 5. Heat exchanger network synthesis

For the improved design described in Section 4, a heat exchanger network shall be developed. To that end the methodology described in Section 2.3 is applied. The network determines the actual utility consumption and thereby allows closing the mass and energy balances of the straw to ethanol process.

When designing the heat exchanger network, some process characteristics have to be considered. The heat exchangers realizing the integration between distillation and evaporation as described in Section 4.1 are prescribed. Due to batch operation the bioreactors (H04–H06) cannot be integrated with other process streams. However, to facilitate a direct comparison of the network with the energy targets developed in Section 3.2, H04–H06 are

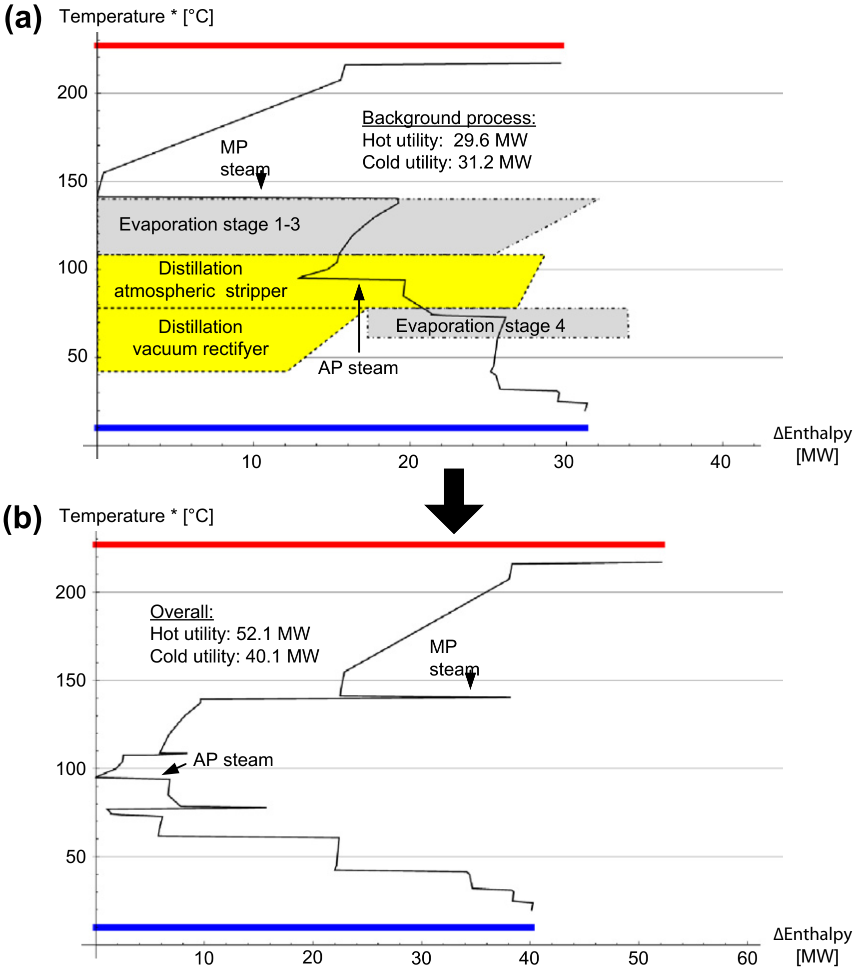

**Fig. 5.** Grand composite curves (GCCs) of the improved case. (a) GCC of background process. Distillation and evaporation are represented separately as boxes. (b) Overall GCC including distillation and evaporation.

included in the problem but excluded from heat exchange with other streams. There are several streams containing water insoluble solids (C01, C03, H03, H09), which can cause difficulties in heat exchangers. Certainly, heat exchange between two streams containing water insoluble solids makes things worse and is consequently forbidden. For similar reasons streams containing insoluble solids are also excluded from heat exchange with the distillation and evaporation sections. The moistened straw entering steam pretreatment (C01) is very high in insoluble solids and consequently poses a particular problem to heat transfer equipment. It is desirable to heat this stream without any further moistening i.e. steam injection. There is equipment available that can fulfill this task [27], however the heat transfer will be lower than in other heat exchangers. Consequently, for this stream the $\Delta T_{\min}$ was set to 25 °C. The stream data of the improved case, as listed in Table 1, was used as input for the heat exchanger network synthesis.

### 5.1. Network for the improved design

The grid diagram of the network resulting from calculations with “TVTHENS” is shown in Fig. 6. With only 14 process–process heat exchangers (HX) a heat recovery of 100 MW is attained. In addition 8 hot utility (HU) and 14 cold utility (CU) heat exchangers with a heat and cooling duty of 61.4 and 49.3 MW have to be implemented. Compared to the targets (see Section 4.1), these values correspond to a very modest increase of only 18% of hot and 23% of cold utility consumption. All process–process and utility heat exchangers are listed in Table 2.

As can be calculated from data in Table 2, the integration of the distillation and evaporation sections with the background process via utilization of MP and AP steam (HX2 and HX3) amounts to 26.4 MW. Adding this value to the 52.2 MW of prescribed integration between the parts of distillation and evaporation (HX12, HX13 and HX14) results in a total heat recovery of 78.5 MW in the distillation and evaporation section. Comparing this value to 61.4 MW of hot utility consumption for the entire network underlines the significance of well-designed solutions for the distillation and evaporation in the process under investigation.

But also the background process’ potential for heat recovery (see Section 3.2) is exploited in the network. Here, a major contribution to heat recovery is achieved through preheating the beer to distillation (C03) using the condensation of the vaporous ethanol product (HX5), condensates from evaporation (HX10 and HX11) and condensed MP steam from pretreatment and drying (HX1). In this way 11 MW of heat can be recovered and hot utility consumption for preheating the beer is reduced by 86%. Thus, only nine heat process–process exchangers are responsible for 90% of heat recovery. Minor contributions to the overall heat recovery are attained through (i) preheating the straw for steam pretreatment (C01) using regenerate from PSA (HX6) and evaporation condensate (HX8), (ii) heating the feed to evaporation (C05) using

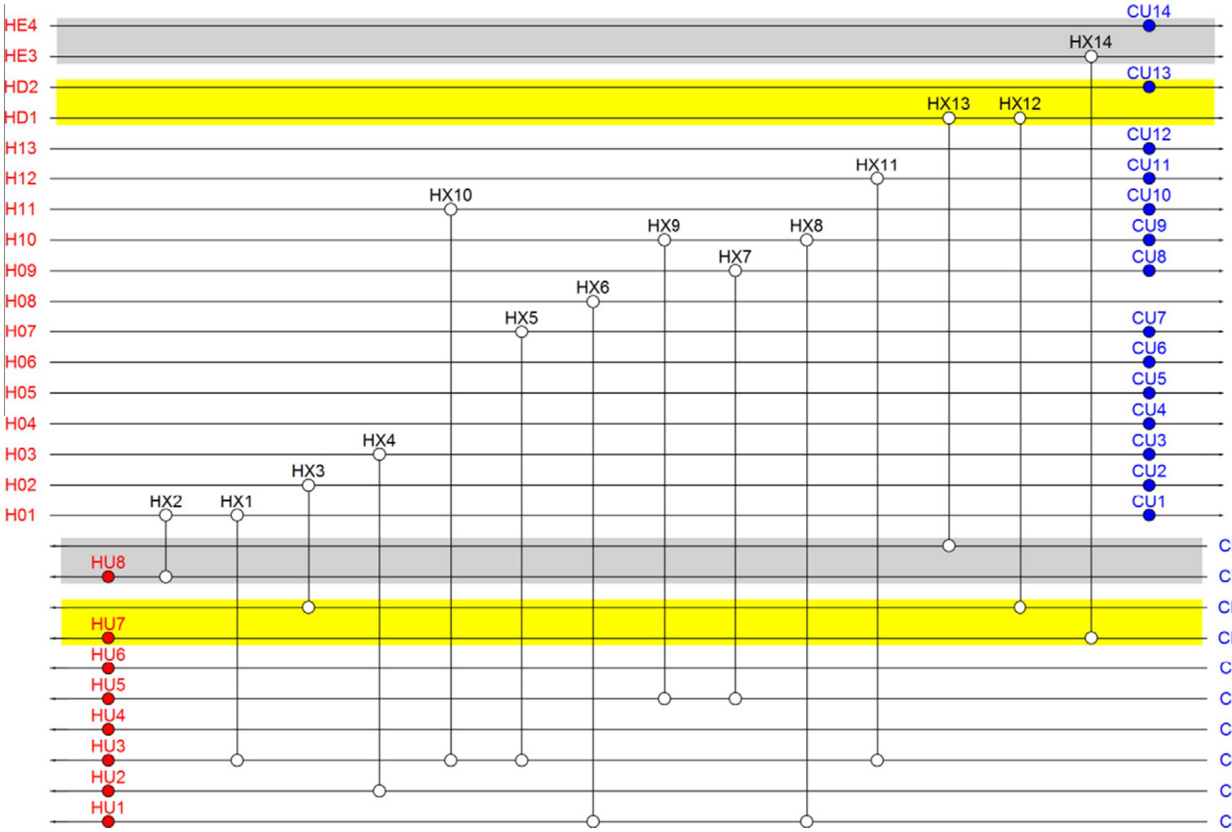

**Fig. 6.** Grid diagram of the network. HX: process–process heat exchanger. HU: hot utility heat exchanger. CU: cold utility heat exchanger. Streams of distillation and evaporation are shown with a shaded background.

the hot stillage (HX7) and evaporation condensate (HX9) and (iii) preheating water, that is used to generate steam for the pretreatment (C02) via the hot slurry obtained from pretreatment (HX4).

Due to unsuitable temperature or technical restrictions some streams cannot be integrated at all and must entirely be covered by utilities. To be specific, these are the cold streams C06 (superheat drying steam) and C04 (vapors to PSA) which both must be superheated well above the pinch and the hot streams H04, H05 and H06 (cooling of bioreactors) that cannot be integrated due to batch operation (see Section 5).

## 6. Discussion

In Fig. 7 the utility consumption of the scenarios is summarized. The base case design of the process was derived from literature and employs efficiently integrated stand-alone solutions for the thermal separation units distillation and evaporation. Via pinch analysis it was found that the base case has a potential for 52 MW or 50% of heat recovery (see also Base case maximum vs. Base case target in Fig. 7). To a large extent this high potential can be attributed to the provision of secondary MP steam by the pretreatment and drying unit operations. The pinch analysis also revealed that AP steam from the pretreatment is not used efficiently in the base case and that a utilization of this heat source could further increase the heat recovery.

Consequently, design modifications of the distillation and evaporation sections were implemented to create an improved design of the process. To be specific, the two sections were integrated by reducing the number of stages and shifting the heat loads to different temperature levels. As a result, the utility targets were reduced by another 9 MW (or ca. 15% of the base case utility targets, see also Fig. 7). It is important to note that the increased heat integration causing this further reduction is twofold: First, between the distillation and evaporation section and second, between the background process and the thermal separation sections. To be specific, AP that could not be utilized in the base case design can be efficiently used to heat the vacuum rectifier or the 4th stage of the evaporation section. It is worth noting that this further utility reduction was achieved even though the process was simplified, namely the number of stages in both the distillation and the evaporation section were reduced. This clearly demonstrates the suitability of the technique applied and the necessity to optimally integrate the thermal separation units with the background process.

For the improved design of the process, a heat exchanger network was developed by simultaneous minimization of utility and heat exchanger cost. With only 14 process–process heat exchanger the obtained network is relatively simple but at the same time guarantees a high heat recovery. The increase of hot and cold utility consumption compared to the improved design targets amount to only 9 MW (or ca. 20% of the improved design utility target, see also Fig. 7). Almost no increase in utility consumption is observed when the base case targets are used as a reference. However, in this context it must be noted that increased heat integration between different sections of the process comes at a price, since it limits process flexibility and operability, especially during startup and maintenance. Ultimately, the question whether the proposed design and network could be implemented in a real facility remains to be answered by more detailed engineering.

The utility requirement of the obtained network allows closing the mass and energy balances of the process. In Table 3 the most prominent mass and energy flows of the process are listed. Comparing the hot utility requirement to the material related energy

**Table 2**
List of heat exchangers in the network. Heat exchanger of the distillation and evaporation sections are shown in bold characters.

| HX Name | Heat (MW) | Hot process streams | | | | Cold process streams | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Stream description | Alias | $T_{in}$ (°C) | $T_{out}$ (°C) | Stream description | Alias | $T_{in}$ (°C) | $T_{out}$ (°C) |
| *Process-process heat exchangers* | | | | | | | | | |
| HX1 | 2.3 | MP steam from SP and dryer | H01 | 145 | 86 | Beer to distillation section | C03 | 76 | 86 |
| **HX2** | **19.3** | **MP steam from SP + dryer** | **H01** | **146** | **145** | **Heat evap. stage 1** | **CE1** | **134** | **135** |
| **HX3** | **7.1** | **AP steam from SP** | **H02** | **100** | **89** | **Reboiler vac. rectifyer** | **CD2** | **72** | **73** |
| HX4 | 2.3 | Slurry from SP | H03 | 99 | 83 | Generate steam for SP | C02 | 15 | 89 |
| HX5 | 3.3 | Ethanol product | H07 | 130 | 78 | Beer to distillation section | C03 | 51 | 65 |
| HX6 | 2.0 | Regenerate from PSA | H08 | 137 | 78 | Straw to SP | C01 | 42 | 57 |
| HX7 | 2.0 | Stillage | H09 | 101 | 91 | Feed to evap. section | C05 | 80 | 91 |
| HX8 | 1.9 | Condensate evap. stage 1 | H10 | 101 | 67 | Straw to SP | C01 | 27 | 42 |
| HX9 | 1.9 | Condensate evap. stage 1 | H10 | 134 | 101 | Feed to evap. section | C05 | 91 | 100 |
| HX10 | 2.6 | Condensate evap. stage 2 | H11 | 124 | 75 | Beer to distillation section | C03 | 65 | 76 |
| HX11 | 3.2 | Condensate evap. stage 3 | H12 | 113 | 47 | Beer to distillation section | C03 | 37 | 51 |
| **HX12** | **10.2** | **Condenser atm. stripper** | **HD1** | **84** | **83** | **Reboiler vac. rectifyer** | **CD2** | **72** | **73** |
| **HX13** | **16.6** | **Condenser atm. stripper** | **HD1** | **84** | **83** | **Heat evap. stage 4** | **CE4** | **73** | **74** |
| **HX14** | **25.3** | **Vapors evap. stage 3** | **HE3** | **114** | **113** | **Reboiler atm. stripper** | **CD1** | **103** | **104** |
| *Hot utility heat exchangers* | | | | | | | | | |
| HU1 | 5.4 | | | | | Straw to SP | C01 | 57 | 99 |
| HU2 | 17.7 | | | | | Generate steam for SP | C02 | 89 | 212 |
| HU3 | 2.2 | | | | | Beer to distillation section | C03 | 86 | 95 |
| HU4 | 0.2 | | | | | Vapors to PSA | C04 | 105 | 130 |
| HU5 | 6.3 | | | | | Feed to evap. section | C05 | 100 | 133 |
| HU6 | 13.5 | | | | | Superheat drying steam | C06 | 150 | 202 |
| **HU7** | **3.3** | | | | | **Reboiler atm. stripper** | **CD1** | **103** | **104** |
| **HU8** | **12.8** | | | | | **Heat evap. stage 1** | **CE1** | **134** | **135** |
| *Cold utility heat exchangers* | | | | | | | | | |
| CU1 | 1.4 | MP steam from SP and dryer | H01 | 86 | 50 | | | | |
| CU2 | 0.5 | AP steam from SP | H02 | 89 | 50 | | | | |
| CU3 | 4.9 | Slurry from SP | H03 | 83 | 45 | | | | |
| CU4 | 1.2 | Yeast production | H04 | 30 | 29 | | | | |
| CU5 | 0.7 | Enzyme production | H05 | 30 | 29 | | | | |
| CU6 | 3.4 | SSCF | H06 | 37 | 36 | | | | |
| CU7 | 0.5 | Ethanol product | H07 | 78 | 30 | | | | |
| CU8 | 2.6 | Stillage | H09 | 91 | 80 | | | | |
| CU9 | 1.8 | Condensate evap. stage 1 | H10 | 67 | 35 | | | | |
| CU10 | 2.1 | Condensate evap. stage 2 | H11 | 75 | 35 | | | | |
| CU11 | 0.5 | Condensate evap. stage 3 | H12 | 47 | 35 | | | | |
| CU12 | 0.9 | Condensate evap. stage 4 | H13 | 66 | 35 | | | | |
| **CU13** | **12.1** | **Condenser vac. rectifyer** | **HD2** | **48** | **47** | | | | |
| **CU14** | **16.8** | **Vapors evap. stage 4** | **HE4** | **73** | **66** | | | | |

MP: medium pressure; SP: steam pretreatment; AP: atmospheric pressure; PSA: pressure swing adsorption; evap.: evaporation; atm.: atmospheric; SSCF: simultaneous sacchrification and co-fermentation; vac.: vacuum.

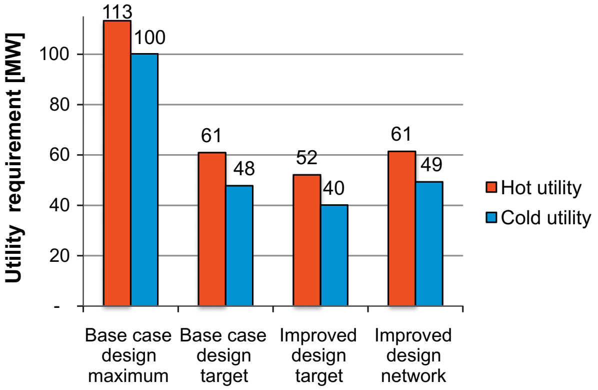

**Fig. 7.** Utility consumption for the different cases.

**Table 3**
Most important mass and energy flows for the process including the hot utility consumption for the non-integrated base case and the network. Material related energy flows are based on the lower heating value (LHV).

| | Mass flow (t/y) | Energy flow (MW) |
|---|---|---|
| Straw (10% DM) | 446,455 | 252 |
| Concentrate (65% DM) | 112,401 | 56 |
| Dried solids (90% DM) | 149,933 | 84 |
| Ethanol | 100,000 | 93 |
| Hot utility base case max. | n.a. | 113 |
| Hot utility network | n.a. | 61 |

flows of the process highlights the significance of heat integration for the prevailing process. The energy contained in residual materials (concentrate and dried solids) sums up to 140 MW, while the maximum hot utility consumption of the base case amounts to 113 MW. Hence, assuming a total efficiency of 85% for steam generation and distribution, the energy contained in the residual materials barely matches the hot utility requirement of the process. On the other hand, for the network developed in this work only 51% of the residual materials suffice to supply the process with heat. The remaining 49% (or 68 MW) can be used for recovery of energy or material by-products. Relating this energy available for by-product recovery to the 93 MW of energy flow of ethanol, the actual product, illustrates the importance of efficient polygeneration concepts. These concepts are necessary to increase the overall efficiency and profitability for ethanol production from straw. In this context, it must be mentioned that within this work we assumed a high conversion of sugars during ethanol fermentation (SSCF); for a lower conversion of sugars efficient polygeneration concepts become even more important.

Some options for polygeneration have been discussed previously [6]. Generally speaking, when assessing different polygeneration concepts, it must be considered that some of these concepts can be designed to perfectly fit to the current process design (e.g. production of electricity or electricity and district heat in a Rankine cycle [6]), whereas other concepts may require a modification of the current process design and integration. The latter is the case for polygeneration concepts that (i) provide heat in excess to the process requirement or at different temperature levels, or for concepts that (ii) do not require some of the process units in the current design (e.g. drying or evaporation). Coproduction of biogas via anaerobic digestion and biogas upgrading to biomethane [6] shall be mentioned as one example for a polygeneration concept that would require a modification of the current design.

## 7. Conclusion

Process simulation and pinch analysis were used to analyze and improve the design of biochemical ethanol production from straw. The analysis was started with a base case design, which was derived from the literature and included multi stage stand-alone solutions for the energy intensive thermal separation units distillation and evaporation. The following can be concluded:

- Energy self sufficient production of ethanol from straw can be realized by utilizing process residues to provide heat.
- Pinch analysis showed that due to highly integrated stand alone solutions for distillation and evaporation on the one hand, and secondary MP steam provided from pretreatment and drying on the other hand, the base case design has a high potential for heat recovery.
- The pinch analysis also revealed that the process design can be improved by adapting the design of the thermal separation units, namely the number of stages, the temperature levels and the heat loads.
- In the improved design thus obtained, further heat recovery and a reduction of the utility requirement were achieved, even though the number of stages in both distillation and evaporation were reduced which demonstrates the suitability of the method applied.
- Optimized stand-alone solutions for the energy intensive multi-stage unit operations are a good starting point in the design procedure; however, for optimal use of process heat, these units must be adapted to the background process.

For the improved design a heat exchanger network was synthesized. Thereto utility and heat exchanger cost were minimized simultaneously. With the network thus obtained, it is possible to determine the actual utility requirement in a possible production facility. Regarding the heat exchanger network the following can be concluded:

- The increase compared of utility requirement compared to the targets is modest, even though a rather simple network was designed.
- This demonstrates the suitability of the approach applied for heat exchanger network synthesis, namely simultaneous minimization of utility and heat exchanger costs.
- For the process under investigation, some 50% of process residues suffice to provide process heat.
- This underlines the importance of efficient polygeneration concepts for ethanol produced from straw.

## 8. Future work

Based on the results of this work, a complete flowsheet model that includes the utility system can be generated. Thereafter further process and energy system analysis such as energy or exergy analysis, techno-economic analysis or life cycle analysis can take place. Based on our findings, we believe that further research shall be dedicated to development of efficient polygeneration concepts, which will lead to higher energy efficiency as well as better economic and environmental performance. When these goals are attained, the production of ethanol from lignocellulosic biomass certainly soon will become a commercial reality.

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# PAPER III PROCESS SIMULATION

Kravanja P. and Friedl A. (2011)

Process simulation of ethanol from straw – validation of scenarios for Austria.

**Chemical Engineering Transaction** 25:863-868

# Process Simulation of Ethanol from Straw – Validation of scenarios for Austria

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In this the work the production of ethanol from straw is assessed from an energetic point of view. For that purpose process simulation with the simulation software IPSEpro is used. For a process based on steam pretreatment and enzymatic hydrolysis, several scenarios for utilization of stillage are simulated. Ethanol yield is 78,3 %, based on C6 sugars in the raw material and overall energy efficiencies range from 38 % to 78 %.

## 1. Introduction

In the EU the target for renewable energy in transport has been defined to be 10 % at 2020 (EU, 2009). Biofuels are one strategy to reach this target and thus biofuels must reach an energy based market share of 5,75 % by 31 December 2010 (EU, 2003). In Austria this share is successfully implemented via blending of diesel with bio-diesel and gasoline with bio-ethanol respectively. Currently ethanol produced from wheat is employed to reach the 5,75 % target as far as gasoline is concerned. In the long run however, the demand for fuels in general and for bio-ethanol in particular will increase consequently new resources for bio-ethanol production have to be tapped.

For two main reasons lignocellulosic materials are a good choice for bio-ethanol production. First, the greenhouse gas mitigation potential compared to both, fossil fuels and bio-ethanol from starchy crops is high (Eisentraut, 2010; Wang et al., 2007) and second usage of additional acreage can be avoided if residual materials from food production or forest industry are employed.

In this work we investigate the production of ethanol from straw from an energetic point of view. Several process scenarios based on steam pretreatment and enzymatic hydrolysis are compared using the steady state process simulation software IPSEpro.

## 2. Process Simulation

For calculation of mass and energy balances the equation oriented, steady state flowsheeting software IPSEpro is employed. A model library for handling the complex materials present in a lignocelluloses to ethanol process was constructed (Schausberger et al., 2010) and is improved and augmented continuously. To guarantee optimal use of energy heat exchanger network synthesis was performed with in-house optimization software.

## 3. Process Description

Figure 1 summarizes the scenarios considered in this work. As can be seen, the scenarios are identical as far as the upstream process, ethanol recovery and stillage separation are concerned.

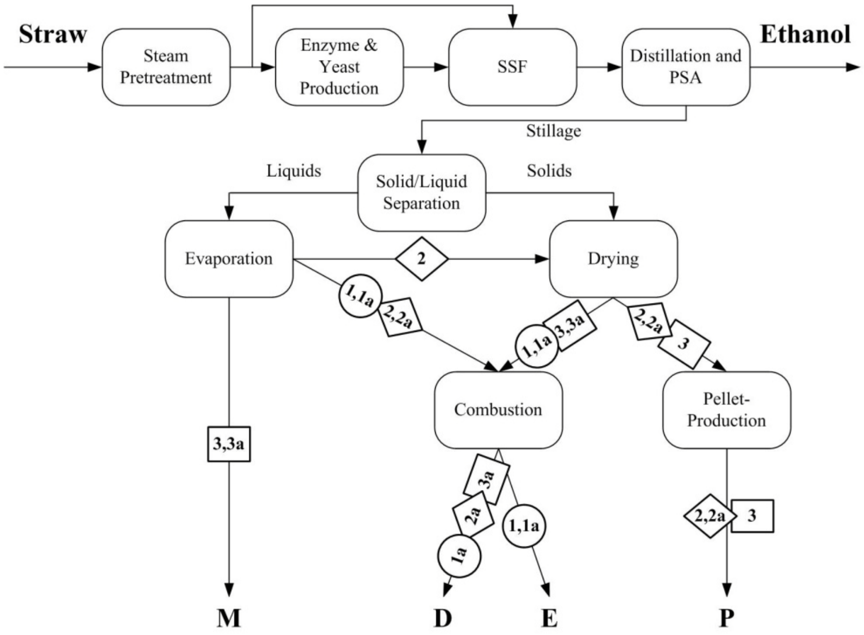

*Figure 1: Schematic summary of process scenarios for the production of ethanol from straw. Byproducts are abbreviated as follows: M:C5-Molasses, D: district heating, E: Electricity, P: Pellets. Lines without numbering are identical in all the scenarios.*

For all the scenarios process steam is generated by burning part of the stillage reducing the processes' demand for fossil energy largely. The remaining streams are used to create the byproducts electricity (E, scenarios 1 and 1a), Pellets (P, 2 and 2a) and C5-molasses (M, 3 and 3a). In scenarios 1a, 2a and 3a additional district heating (D) is produced. Ethanol production capacity is 100000 t/y, operating time is 8000 h/y.

### 3.1 Steam Pretreatment

Baled straw with a moisture content of 10 %(w/w) is shredded to smaller pieces, wetted to reach a moisture content of 65 %(w/w) and preheated close to the boiling temperature of water. The moistened and preheated straw is impregnated with 1 %(w/w) $SO_2$ based on dry matter. Subsequent steam pretreatment is performed at 190 °C. Heat losses are assumed to be 10 % of total heat transferred. As suggested by Wingren (Wingren et al., 2003) the pressure release after steam pretreatment is performed in two steps, first at 4 bar and then at 1 bar. In steam explosion, 80 % of hemicelluloses sugars are released as sugar monomers, 15 % are degraded. For cellulose 10 % and 2 % of sugars are released as monomers and degraded, respectively. Formation of sugar oligomers is not considered.

### 3.2 Simultaneous saccharification and fermentation, enzyme production and yeast propagation

The slurry after steam pretreatment is neutralized using $NH_4(OH)$, cooled and split into three streams. The major part is directly fed to simultaneous saccharification and fermentation (SSF) and minor parts are used for enzyme production (EP) and yeast propagation (YP). The massflows of the streams to EP and YP are a result of the conversions in the reactors on the one hand and enzyme and yeast requirements in SSF on the other hand.

In YP the pretreated straw is enriched with molasses to reach approximately equal amounts of C6 sugars from straw and molasses respectively. Moreover corn steep liquor (CSL) and Diammiumphosphate (DAP) are added as nutrients. 60 % of C6 sugars fed to yeast propagation are converted to yeast and 35 % are converted to $CO_2$ and $H_2O$, corresponding to a biomass/sugar yield of approximately 0,5 kg/kg.

In contrast to yeast *T.reesei* can also utilize C5 sugars, hemicelluloses and cellulose. Consequently no molasses but only CSL and DAP are added to the pretreated slurry. In EP 50 % of carbohydrates are converted to $CO_2$ and $H_2O$, 35 % are converted to enzyme and 10 % are converted to biomass, corresponding to an enzyme/sugar yield of 0,28 kg/kg. Specific enzyme activity is assumed to be 600 FPU/g Enzyme.

SSF is performed for 72 h at 37 °C and 12 %(w/w) water insoluble solids (WIS) with an enzyme loading of 15 FPU/g cellulose and an initial yeast concentration of 2 g/l. Cellulose to C6 conversion and C6 to Ethanol conversion are both set with 92 %, yielding a final ethanol concentration of approximately 4 %(w/w). Again, CSL and DAP are added to meet the yeast's requirements.

### 3.3 Ethanol recovery and purification

For ethanol recovery two parallel stripper columns and one rectifier column as suggested by Wingren (Wingren et al., 2008) are used. Evaporation in the bottom of the high-pressure stripper takes place at 133 °C and condensation in the head of the rectifier at 54 °C. The 92,5 %(w/w) ethanol head product is compressed, superheated to 130 °C and sent to pressure swing adsorption (PSA). In PSA ethanol is purified to 99,5 %(w/w). 25 % of the purified ethanol are used for recovery of the loaded bed and thereafter returned to the rectifier. Purified ethanol is condensed and cooled to 30 °C.

Ethanol containing vapors from SSF and ethanol condensation are sent to the scrubbing system. In accordance with emission standards for volatile organic carbon (VOC) final ethanol concentration in the vapors leaving the scrubber are set to reach 100 mg $C/Nm^3$.

### 3.4 Stillage utilization

The stillage from distillation containing all the solids, water and byproducts of prior conversion steps is sent to a filter press, separating liquids and soluble solids from insoluble solids. The drymatter content of the insoluble solid stream is assumed to be 50 % (w/w), corresponding to a WIS content of approximately 41 % (w/w). Retention for insolubles is assumed to be 99 %. The liquid fraction containing most of the soluble solids is concentrated in a 5 effect evaporation train working in co-current mode. A part of the vapors from evaporation is recycled, the rest is disposed of. Insoluble Solids are dried to 90 % drymatter in a superheated steam dryer, working at 4 bar.

Now several ways to utilize the residual streams exist, as indicated by the numbers 1 through 3a in Figure 1. For all of the scenarios a part of the residual streams is burnt in a boiler to provide process steam at two levels. The boiler is operated at 820 °C with air recirculation and a lambda of 1,7. Flue gas temperature is 120 °C or 130 °C (depending on scenario), resulting in a boiler efficiency of approximately 88 %.

### 3.4.1. Combined heat and Power

In scenarios 1 and 1a the dried insoluble solids as well as the concentrated soluble are burnt in a boiler. Steam is produced at 63 bar and 650 °C and expanded in a turbine to produce electricity for the process. Excess electricity can be sold to the grid. Process steam is extracted at the two pressure levels required. Isentropic and mechanical turbine efficiency are 87 % and 97 %, respectively. Electric and mechanical generator efficiency is 97 %. In scenario 1 wet steam coming from the turbine is condensed at 50 °C using cooling water. In scenario 1a steam is condensed at higher temperature and together with high temperature cooling water of the ethanol process used for district heating. Supply and return temperature of the district heating system are 110 °C and 50 °C, respectively.

### 3.4.2. Pellets

In scenarios 2 and 2a process electricity is supplied from the grid. The dried insoluble solids are pelletized and can be sold as solid fuel. Since the energy content of the concentrated soluble solids is more than sufficient to meet the processes heat demand, two options for excess solubles are possible. In scenario 2 excess solubles are dried and pelletized together with the insoluble solids. In scenario 2a all the solubles are burnt, excess heat and high temperature cooling water of the ethanol process are used for district heating.

In scenario 2C5 (not explicitly included in Figure1) it is assumed, that yeast can co-ferment C5 sugars to produce ethanol. Conversions of C5 to ethanol and biomass are 75 % and 5 %, respectively. All the solids are dried and the amount required to meet the processes' heat demand is burnt, excess solids are pelletized.

### 3.4.3. C5-Molasses

In scenarios 3 and 3a process electricity is supplied from the grid. The dried solids are used as fuel for the boiler, whereas the concentrated solubles (C5 sugars and other soluble components) can be sold as a product. One possible use is feed for animals (Larsen et al., 2008). Since the energy content of the dried solids exceeds the processes heat demand, excess solids can be either pelletized (scenario 3) or used to produce district heating (scenario 3a, see also sections 2.4.1 and 2.4.2).

## 4. Results and Discussion

Table 1 summarizes most important mass and energy flows for the scenarios. In all the cases, except 2C5 ethanol yield is 0,171 kg/kg, corresponding to 78,3 % of theory, based on C6 sugars in the raw material. In case 2C5 ethanol yield is 0,249 kg/kg dry, corresponding to 70,4 % of theory based on C5 and C6 sugars in the raw material.

*Table 1: Summary of mass and energy flows for the scenarios, all massflows are 100 % drymatter. Abbreviations: E: Electricity, EtOH: Ethanol, M:C5-Molasses, P: Pellets, D: district heating*

| | 1 | 1a | 2 | 2C5 | 2a | 3 | 3a |
|---|---|---|---|---|---|---|---|
| Straw In [t/y] | 583.257 | 583.257 | 583.257 | 401.809 | 583.257 | 583.257 | 583.257 |
| E In [MW] | - | - | 8,9 | 9,0 | 8,9 | 8,8 | 8,9 |
| EtOH Out [t/y] | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 |
| M Out [t/y] | - | - | - | - | - | 191.850 | 191.850 |
| P Out [t/y] | - | - | 245.118 | 108.615 | 188.495 | 55.290 | - |
| D Out [MW] | - | 125,3 | - | - | 72,5 | - | 68,9 |
| E Out [MW] | 47,4 | 38,1 | - | - | - | - | - |

Figure 2 shows the energy balance for the scenarios (for material flows the lower heating is used to derive energy content). Energy outputs are expressed as percentage of energy in inputs. In cases 1 and 1a, straw is the only energy input, whereas in cases 2 through 3a electricity is also considered as input. For scenarios where only C6 sugars are utilized for ethanol production, 25 % (2, 2a ,3 ,3a) to 26 % (1,1a) of energy input is recovered in ethanol, whereas for case 2C5 36 % of energy input is contained in ethanol.

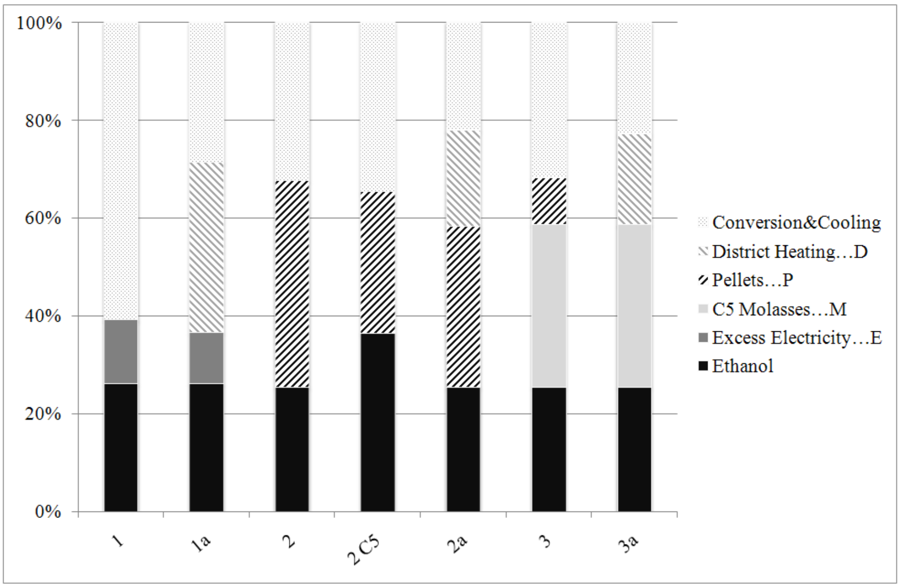

*Figure 2: Energy balance for the production of Ethanol from Straw, expressed as percentage of energy inputs straw (cases 1 and 1a) and straw + electricity (other cases).*

As can be seen, total process efficiency ranges from 38 % for case 1 to 78 % cases 2a and 3a. As generally known utilization of off-heat for district heating (1a, 2a, 3a) leads to high efficiency processes, demand for district heating however is limited and strongly dependent on plant-location. From an energetic point of view the relatively low efficiency for cases where electricity is produced on-site (1, 1a) favors scenarios 2, 2a, 3 and 3a.

## 5. Conclusions and Outlook

Several scenarios for the production of ethanol from straw where investigated from an energetic point of view, using process simulation. For all the scenarios, process heat demand is supplied by burning residual materials. Process electricity is produced on-site or purchased. With overall energy efficiency between 38 % and 78 % the production of ethanol of straw is a highly efficient process.

Future work will be dedicated to economic evaluation and life cycle analysis, determining socio-economic perspectives of the technology.

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# PAPER IV PROCESS SIMULATION

Lassmann T., Kravanja P. and Friedl A. (2011)

Prozess-simulation der Produktion von Ethanol und Methan aus lignocellulosehaltigen Rohstoffen (in german).

**Chemie Ingenieur Technik** 83(10):1609-1617

Forschungsarbeit

# Prozesssimulation der Produktion von Ethanol und Methan aus lignocellulosehaltigen Rohstoffen

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**DOI:** 10.1002/cite.201100090

Die Stoffstrom- und Energieanalyse mittels Prozesssimulation gibt einen guten Einblick in die Möglichkeiten der kombinierten Produktion von Ethanol und Methan. Eine Beschreibung des Gesamtprozesses, inklusive der gewählten Annahmen für die Simulation, bildet die Basis für die Bilanzierung. Es wird gezeigt, dass man annähernd 650 000 $t\,a^{-1}$ Stroh (90 % Trockensubstanz, TS) bzw. 870 000 $t\,a^{-1}$ Fichte (45 % TS) benötigt um 100 000 $t\,a^{-1}$ Ethanol zu erzeugen. Der Biogasertrag für Stroh ist dabei mit $84{,}5 \cdot 10^6\,Nm^3a^{-1}$ deutlich größer als der Ertrag aus Holz ($22{,}5 \cdot 10^6\,Nm^3a^{-1}$). Um die Effizienz der beiden Prozessvarianten vergleichen zu können, wird mittels energetischer Analyse der Wirkungsgrad berechnet, wobei sich für den Stroh-Prozess ein etwas höherer Wert ergibt als für Fichte.

**Schlagwörter:** Ethanol, Methan, Prozesssimulation, Stoffbilanz

*Eingegangen:* 31. Mai 2011; *revidiert:* 12. Juli 2011; *akzeptiert:* 14. Juli 2011

## Process Simulation of Ethanol and Methane Production from Lignocellulosic Raw Materials

Using process simulation for material flow and energy analysis gives a good insight into the possibilities of a combined ethanol and methane production. A description of the overall process, including all assumptions for simulation, serves as basis for mass and energy balances. It is shown that approximately 650 000 $t\,a^{-1}$ straw (90 % dry matter, DM) or 870 000 $t\,a^{-1}$ spruce (45 % DM) is needed to produce 100 000 t of ethanol per year. Straws biogas yield accounts for $84.5 \cdot 10^6\,Nm^3a^{-1}$, which is many times more than the $22.5 \cdot 10^6\,Nm^3a^{-1}$ obtained by spruce. An energetic analysis is used to calculate the respective efficiency of the two process options whereas straw results in a slightly better value than spruce.

**Keywords:** Ethanol, Mass balance, Methane, Process simulation

## 1 Einleitung

Seit einigen Jahren genießt die Produktion von Treibstoff-Ethanol aus erneuerbaren, lignocellulosen Materialen international große Aufmerksamkeit von Forschung, Politik und Industrie. In Österreich haben hierbei Fichtenholz und Stroh von Weizen und Mais das höchste Potenzial [1]. Neben den günstigen Eigenschaften als Otto-Brennstoff liegt das große Interesse vor allem an der Umgehung der „Teller-Tank-Diskussion“ sowie an dem hohen $CO_2$-Einsparungspotenzial der Technologie. Allerdings stellen lignocellulosehaltige Rohstoffe technologisch eine besondere Herausforderung für die biotechnologische Produktion von Ethanol dar. Einerseits sind die Zucker der Cellulose und Hemicellulose wesentlich schwieriger zugänglich als z. B. die Zucker von Stärke oder Zuckersaft. Andererseits ist der Gehalt an Zuckern im Rohstoff geringer als bei den konventionellen Rohstoffen, was zur Folge hat, dass ein großer Anteil der Energie des Rohstoffs nach Fermentation und Abtrennung des Ethanols in der Schlempe verbleibt. Diese Rückstände dienen üblicherweise zur Bereitstellung der Prozessenergie. Eine gezielte Nutzung dieser Stoffströme zur Gewinnung zusätzlicher Energieträger ermöglicht es jedoch, den Prozess wesentlich effizienter zu betreiben.

Die Herstellung von Biogas mittels anaerober Fermentation der Schlempe und anschließendem Upgrade zu Biome-

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than bietet hier vielversprechende Möglichkeiten. Trennt man die schwer vergärbaren, unlöslichen Feststoffe vor der anaeroben Fermentation ab, so kann diese zusätzlich zur Gewinnung eines etablierten gasförmigen Produkts auch als Vorreinigung für eine aerobe Abwasserreinigung dienen. Letztere ist wiederum nötig um Prozesswasser rückführen zu können und den Frischwasserbedarf zu minimieren. Somit kann eine energieintensive Eindampfung zur Schließung des Wasserkreislaufs entfallen.

In dieser Arbeit werden mittels Prozesssimulation die Möglichkeiten einer kombinierten Produktion von Ethanol und Biogas aus Holz bzw. Stroh betrachtet. Eine detaillierte Bilanzierung sowie die Analyse der Mengen- und Energieströme zeigt dabei einerseits Möglichkeiten zur effizienten Nutzung des gesamten Rohstoffs auf. Andererseits gibt sie Einblicke in technische Details und deckt dabei mögliche Hindernisse einer großtechnischen Umsetzung der Technologie auf.

## 2 Rohstoffe: Stroh und Holz

Die unterschiedliche Zusammensetzung von Stroh und Holz ist in Tab. 1 erkennbar. Als Hexosane werden alle in der Celluose und Hemicellulose vorkommenden Poly-C6-Zucker bezeichnet, Pentosane beschreiben die Poly-C5-Zucker und im Rest kommen unter anderem die Asche, Proteine und Extraktstoffe vor. Die in der Tab. 1 angegebenen Werte, sind intern angenommene und wurden aus dem Mittel mehrerer Quellen gebildet. Mit 58 % Hexosanen, hat Fichte gegenüber Stroh den Vorteil, dass weniger Einsatzstoff benötigt wird um bei gleicher Ausbeute eine bestimmte Menge an Ethanol zu produzieren. Der höhere Ligninanteil macht Holz jedoch härter und widerstandsfähiger, was sich in harscheren Vorbehandlungsbedingungen niederschlägt. Da die Fermentation von C5-Zuckern zu Ethanol noch nicht Stand der Technik ist, birgt die höhere Menge an C5-Zuckern im Stroh – 23 % im Vergleich zu 8 % für Fichte – ein höheres Potenzial für die Biogas-Erzeugung. Der größte Nachteil von Stroh gegenüber Holz liegt jedoch im 20-%igen Anteil an Reststoffen, da deren Hauptkomponente die Asche ist.

Sämtliche für die Energiebilanz notwendigen Biomasse-Heizwerte wurden nach dem PLS-Modell von Friedl [2] berechnet. Für das frische Stroh (90 % TS) ergibt sich ein unterer Heizwert (LHV) von 15 991 kJ kg$^{-1}$ und für das trockene Stroh ein Wert von 18 040 kJ kg$^{-1}$. Der LHV der Fichte beträgt bei einem Feuchtegehalt von 45 % TS 7254 kJ kg$^{-1}$ und im trockenen Zustand erhöht sich dieser Wert auf 19 106 kJ kg$^{-1}$.

**Tabelle 1.** Zusammensetzung von Stroh und Holz im Vergleich. Gemittelte Werte einer intern durchgeführten Analyse zahlreicher Literaturstellen.

| | Zusammensetzung [Gew.-%] | |
|---|---|---|
| | Stroh | Fichte |
| Hexosane | 39 | 58 |
| Pentosane | 23 | 8 |
| Lignin | 18 | 29 |
| Rest | 20 | 5 |

## 3 Prozessbeschreibung

Der für die Stoffstromanalyse untersuchte Prozess ist schematisch in Abb. 1 dargestellt und ist für beide Einsatzstoffe identisch. Als Ausgangssituation wurde angenommen, dass die jährliche Produktion 100 000 t Ethanol bei 8000 Betriebsstunden pro Jahr beträgt. Alle Annahmen für den Prozess sind in Tab. 2 aufgelistet.

### 3.1 Ethanol-Prozess

### 3.1.1 Vorbehandlung, Enzym- und Hefeproduktion

Um die Biomasse, in diesem Fall Holz bzw. Stroh, für einen enzymatische Aufschluss zugängig zu machen, bedarf es einer mechanischen Zerkleinerung und anschließender chemischer Vorbehandlung. Eines der gängigsten Verfahren für letzteres ist die sogenannte Steam Explosion (SE), bei der $SO_2$ eingesetzt wird. Das zerkleinerte Stroh wird zunächst durch Zugabe von Wasser auf einen Feuchtegehalt von 65 Gew.-% gebracht. Dies ist für das Holz nicht erforderlich, da es bereits einen Feuchtegehalt von 55 Gew.-% besitzt. Anschließend erfolgt eine Vorheizung bis zur Siedetemperatur des Wassers und die Zugabe des $SO_2$ (s. Tab. 2). Die Vorbehandlung für Stroh und Holz unterscheidet sich im Wesentlichen dadurch, dass die SE für Holz mehr $SO_2$ benötigt und wegen der besseren Ausbeuten in zwei Schritten mit ansteigender Temperatur durchgeführt wird [3]. In beiden Fällen wird ein Großteil der Hemicellulose aufgeschlossen, die Cellulose nur teilweise und das Lignin nicht umgesetzt [1]. Die genauen Prozessparameter und unterschiedlichen Umsatzraten sind in Tab. 2 angegeben. Für detaillierte Information über diesen Teilprozess und dessen Parameter siehe [1].

Die Biomasse wird nach der Vorbehandlung mit $NH_4(OH)$ neutralisiert und gekühlt. Ein kleiner Teil davon wird zur Enzym- bzw. Hefeproduktion (YP) verwendet, der Großteil geht in die Ethanol-Erzeugung. Bei der Hefeproduktion wird das vorbehandelte Stroh mit Molasse versetzt und die Zugabe von Maisquellwasser (CSL) und Diammoniumphosphat (DAP) dient der Nährstoffanreicherung. Es wird eine Hefeausbeute von 0,5 kg Hefe pro umgesetztem kg Kohlenhydrat angenommen [1]. Für die Enzymproduktion (EP) wird eine Enzymausbeute von 0,28 kg kg$^{-1}$ und eine spezifische Aktivität der Enzyme von 600 FPU g$^{-1}$ Enzyme nach [1] veranschlagt.

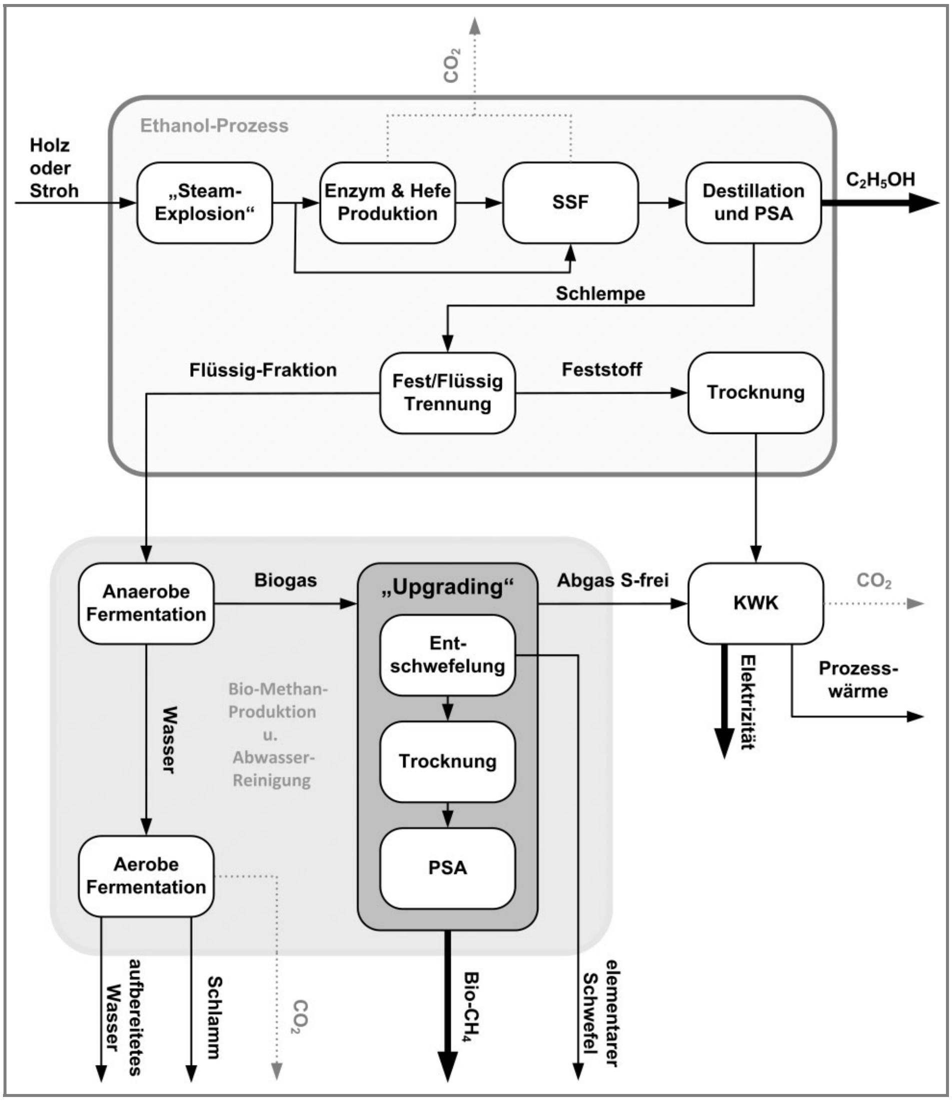

**Abbildung 1.** Fließbild des Ethanol-Prozesses für Holz oder Stroh, bestehend aus drei Teilprozessen: Ethanol-Herstellung, Biomethan-Produktion und KWK-Anlage.

### 3.1.2 Hydrolyse und Fermentation

Für den nachfolgenden enzymatischen Aufschluss werden Hydrolyse und Fermentation in einem Schritt durchgeführt, was als Simultaneous Saccharification and Fermentation (SSF) bezeichnet wird. Dies scheint zurzeit eine der vielversprechendsten Varianten zu sein [4, 5]. Im Hydrolyse-Schritt wird die Cellulose zu Zucker umgewandelt und anschließend zu Ethanol fermentiert. Hefe (*S. cerevisiae*) hat sich bei der Ethanolherstellung aus zucker- oder stärkehältigen Materialien bereits etabliert, im Lignocellulose-Prozess hat sie jedoch den Nachteil, dass die C5-Zucker wie Xylose und Arabinose nicht umgesetzt werden können. Die Umsatzraten für Cellulose und Zucker sowie der Feststoffgehalt sind in Tab. 2 aufgeführt. Die SSF erfolgt bei einer Temperatur von 37 °C, einer Verweilzeit von 72 h und einer Enzymbeladung von 15 FPU $g^{-1}$ Cellulose [1].

### 3.1.3 Destillation

Im Destillationsschritt wird das Ethanol von den anderen Komponenten getrennt und tritt als azeotropes Gemisch am Kopf der Kolonne aus. Dieser Aufbereitungsschritt ist sehr energieintensiv und bedarf einer internen Nutzung der Wärme. Anschließend absolutiert man das Ethanol/Wasser-Gemisch mittels Druckwechsel-Adsorption (PSA) auf den gewünschten Ethanol-Gehalt von 99,5 Gew.-%. Bei der Destillation fällt auch ein Rückstand an, die sogenannte Schlempe. Diese ist eine Suspension bestehend aus Wasser, Lignin und anderen nichtverwerteten organischen Komponenten der SSF. Die Schlempe wird nachfolgend einer Fest/Flüssig-Trennung unterzogen, wodurch sie in unlösliche Feststoffe und eine lösliche Substanzen enthaltende Flüssigfraktion aufgeteilt wird. Die Feststoffe, deren Hauptbestandteil Lignin ist, werden nach einem Trocknungs-

**Tabelle 2.** Parameter und Annahmen für die kombinierte Produktion von Ethanol und Biomethan.

| | Stroh | Holz |
|---|---|---|
| *Steam Pretreatment* | | |
| Temperatur[1] [°C] | 190 | 190 + 210 |
| $SO_2$ in Vorbehandlung[2] [Gew.-%] | 1 | 2,5 |
| Hemicellulose → Zucker [%] | 80 | 85 |
| Hemicellulose → Abbauprodukte [%] | 15 | 10 |
| Cellulose → Zucker [ %] | 10 | 35 |
| Cellulose → Abbauprodukte [%] | 2 | 5 |
| *Enzymproduktion* | | |
| Enzymausbeute $Y_{E/S}$[3] [–] | 0,28 | |
| Substratumsatz [ %] | 95 | |
| spezifische Aktivität Enzym [FPU $g^{-1}$] | 600 | |
| *Hefeproduktion* | | |
| Hefeausbeute $Y_{X/S}$ [4] [–] | 0,5 | |
| Substratumsatz [%] | 95 | |
| *SSF* | | |
| Feststoffgehalt (WUF)[5] [Gew.-%] | 12 | 10 |
| Cellulose → Ethanol [%] | 85 | |
| C6-Zucker → Ethanol [%] | 92 | |
| Enzym-Beladung [FPU $g^{-1}$ Cellulose] | 15 | |
| Verweilzeit [h] | 72 | |
| Reaktorvolumen [$m^3$] | 22 600 | 20 100 |
| *Biogasproduktion und Upgrading* | | |
| CSB-Fracht [kg $s^{-1}$] | 11,3 | 3,1 |
| CSB-Konzentration [g $L^{-1}$] | 130 | 40 |
| S/CSB im Feed [g $kg^{-1}$] | 7 | 42 |
| $H_2S$ im Rohgas [Vol.-%] | 0,76 | 4,1 |
| Raumbelastung CSB [kg $m^{-3}d^{-1}$] | 20 | |
| Reaktorvolumen[6] [$m^3$] | 48 800 | 13 000 |
| Verweilzeit [Tage] | 6,5 | 2 |
| Benötigte $H_2S$-Entfernung [%] | 99,95 | 99,99 |
| Methanverlust PSA [%] | 3 | |
| Methangehalt Produktgas [Vol.-%] | 98 | |
| *KWK-Anlage* | | |
| Heißgastemperatur [°C] | 820 | |
| Abgastemperatur [°C] | 120 | |
| Primärdampf | 650 °C, 64 bar | |
| Entnahmedampf Hoch [bar] | 20 | |
| Entnahmedampf Niedrig [bar] | 4 | |
| isentroper Wirkungsgrad Turbine | 0,87 | |
| mechanischer Wirkungsgrad Turbine | 0,98 | |

[1] stufige Vorbehandlung; [2] bezogen auf trockene Biomasse; [3] kg Enzym produziert pro kg Kohlenhydrat umgesetzt; [4] kg Hefe produziert pro kg Kohlenhydrat umgesetzt; [5] wasserunlösliche Feststoffe OLR 20, CSB-Abbau 75 %, 80 % S aus Vorbehandlung in Flüssigfraktion, [6] Schlempevolumen × Verweilzeit (kein Aufschlag).

schritt in der Kraft-Wärme-Kopplungs(KWK)-Anlage zur Prozessdampf- und Prozessstromerzeugung genutzt.

Bei bisherigen Prozessen wurde die Flüssigfraktion einer mehrstufigen Eindampfung unterzogen. Das dabei entstandene Kondensat wurde in den Prozess rückgeführt und das Konzentrat zur energetischen oder stofflichen Nutzung herangezogen [6 – 8]. Dies ist aus energetischer Sicht eher nachteilig, da bei einer mehrstufigen Eindampfanlage viel Primärdampf benötigt wird um Wasser zu verdampfen und ein Konzentrat zu erzeugen. Es ist daher nicht abwegig, die an organischen Substanzen reichhaltige Flüssigfraktion zur Biogaserzeugung zu nutzen.

## 3.2 Biomethan-Produktion und Abwasserreinigung

Neben Ethanol zusätzlich noch Biogas als zweites Hauptprodukt zu erzeugen, ermöglicht eine etwas variablere Prozessführung. Die ungenutzten Zucker aus der SSF, sowie Proteine und Extrakte können somit in der Biogaserzeugung verwertet werden, wodurch eine kaskadische Nutzung der Zucker entsteht. Der Teilprozess der Biomethan-Produktion und Abwasserreinigung besteht aus einer anaeroben Fermentation mit nachfolgender Aerob-Stufe zur Wasseraufbereitung und einem Biogas-Aufbereitungsschritt zu Biomethan (s. Abb. 1).

Durch anaerobe Fermentation werden die organischen Substanzen aus der Flüssigfraktion der Schlempe zur Biogaserzeugung genutzt. Der CSB (chemischer Sauerstoffbedarf) gibt dabei Auskunft über die Menge an Sauerstoff, die benötigt wird um alle organischen Substanzen zu oxidieren und ist somit ein Maß für die Menge an fermentativ abbaubaren Substanzen. Es wird angenommen, dass 75 % CSB zu Biogas, 15 % CSB zu Schlamm und 10 % CSB nicht verwertet werden, wobei die Berechnung nach Buswell [9] erfolgt. Die spezifische Schlammbildung beträgt dann ca. 0,15 kg $kg^{-1}$ CSB-abgebaut, was in der Literatur die Obergrenze darstellt [10]. Um eine gut funktionierende anaerobe Fermentation sicherstellen zu können wird festgelegt, dass der Stickstoffgehalt mindestens 10 $g_N kg^{-1}$ CSB bzw. der Phosphorgehalt mindestens 1,25 $g_P kg^{-1}$ CSB betragen muss.

Bei der Biogas-Produktion wird bei beiden Rohstoffen eine Raumbelastung von 20 $kg_{CSB} m^{-3} d^{-1}$ angenommen. Dieser Wert ist jedoch nur bei der Umsetzung in einem Reaktor mit Schlammrückhalt, wie z. B. einem UASB-Reaktor, zu erzielen. Eine Literaturrecherche hat für den Fall Stroh noch keine genaue Aussage über die tatsächlich erreichbaren Werte ergeben. Melasse aus Zucker hat eine sehr ähnliche Zusammensetzung und für diese wurden bereits Werte über 20 $kg_{CSB} m^{-3} d^{-1}$ erreicht [11, 12]. Diese Annahme scheint für die Berechnung sehr realistisch, eine genaue Überprüfung mittel Laborversuchen wäre aber anzuraten. Über die gewählte CSB-Raumbelastung kann somit das erforderliche Reaktorvolumen ermittelt werden [12].

### 3.2.1 Schwefelbeladung der Anaerobstufe und $H_2S$-Bildung

Schwefel ist auch in diesem Prozess ein Problemstoff, der aufgrund des $SO_2$-Einsatzes in der Vorbehandlung auftritt, und hat bei der Biogasfermentation die folgenden zwei Effekte: Erstens ist die $H_2S$-Bildung gegenüber der $CH_4$-Bildung thermodynamisch bevorzugt, d. h. Schwefel im Substrat hat eine Reduzierung der $CH_4$-Ausbeute zur Folge. Zweitens erfolgt eine Sulfid-Inhibition, d. h. das entstehende $H_2S$ hemmt die Methanbakterien [13]. Bei einem S/CSB-Verhältnis kleiner $33{,}3\,g_S kg_{CSB}^{-1}$ (entspricht $CSB/SO_4 > 10$) tritt keine $H_2S$-Inhibition ein, ab einem S/CSB-Verhältnis von $670\,g_S kg_{CSB}^{-1}$ (entspricht $CSB/SO_4 < 0{,}5$) ist diese jedoch sicher [11].

### 3.2.2 Biogas-Aufbereitung

Die Aufreinigung des Rohbiogases auf Erdgasqualität wird als *Upgrading* bezeichnet. Dabei sind folgende Prozessschritte nötig: Entschwefelung, Trocknung und PSA. Da die PSA auf die Trennung von $CH_4$ und $CO_2$ ausgelegt ist, müssen die Eingangskonzentrationen auf $5\,mg\,m^{-3}$ Schwefelgehalt und 0,15 Vol.-% Wassergehalt gebracht werden [14]. Um mittels biologischem Verfahren das Biogas auf Erdgasqualität zu bringen ist ein Biowäscher mit externer Waschwasserregenerierung am besten geeignet, der aus einem Gegenstromabsorber und einem separaten Bioreaktor besteht [14]. Mit diesem Verfahren ist es möglich eine Lufteinbringung in den Biogasstrom zu verhindern und auch eine Verblockung des Wäschers kann somit ausgeschlossen werden [14]. Die Firma Paques gibt an, dass mit dem THIOPAQ®-Prozess mehr als 99,8 % des Schwefels entfernt werden können [15].

Im THIOPAQ®-Prozess strömt das $H_2S$-reiche Gas von unten in den Wäscher, das $H_2S$ wird von der alkalischen Flüssigkeit absorbiert, während im Kopf des Wäschers das schwefelfreie Biogas austritt. Die $H_2S$-haltige Flüssigkeit fließt in den Bioreaktor, wo ein spezielles Bakterium in Kombination mit einem gewissen Volumenstrom zugeführter Luft dafür sorgt, dass dieser oxidiert wird. Der Schwefel kann nun mittels Zentrifugieren oder einem Bandfilter noch weiter entwässert werden. Die schwefelfreie Flüssigkeit aus dem Bioreaktor wird wieder dem Absorber rückgeführt. Der abgetrennte Schwefel kann in weiterer Folge als Düngemittel oder als Pflanzenschutzmittel eingesetzt werden.

Die Gastrocknung erfolgt mittels Gaskühlung, wodurch sich der Wasserdampfanteil in Biogasen bis kleiner 0,15 Vol.-% reduzieren lässt [14]. Dieser Teilschritt ist äußerst wichtig, da eine Kondensatbildung und die damit einhergehende Korrosion in den nachfolgenden Schritten vermieden werden.

Adsorption bei höherem Druck, Desorption durch Druckabsenkung im Gleich- bzw. Wechselstrom, Desorption durch Spülen mit Roh- oder Produktgas und Druckaufbau mit Roh- oder Produktgas sind die vier Teilschritte des PSA-Verfahren. Es ist eines der gängigsten Verfahren zur $CO_2$-Abtrennung und ein Methanverlust von weniger als 2 % kann erreicht werden [14]. Das Abgas wiederum wird anschließend gemeinsam mit den Feststoffen aus der Trocknung verbrannt (s. Abb. 1). Für die Biogas-Aufbereitung wird angenommen, dass 3 % des Methans über das Abgas verloren gehen. Der spezifische elektrische Energieeintrag der PSA, wird nach ISET [16] mit einem Wert von $0{,}25\,kWh\,Nm^{-1}$ Rohgas festgelegt.

### 3.2.3 Abwasserreinigung

Das von Anaerobschlamm befreite Abwasser wird einer Aerob-Stufe zugeführt. Bei der aeroben Fermentation reagieren die im Abwasser enthaltenen organischen Bestandteile mit dem Sauerstoff aus der Begasungsluft. Die anwesenden Mikroorganismen wirken dabei als Katalysatoren, wodurch eine Umsetzung des organischen Kohlenstoffs der Edukte zu 50 % $CO_2$ und 50 % Biomasse erfolgt. Somit entsteht zusätzliche Biomasse, der sogenannte Aerobschlamm [17].

### 3.3 Kraft-Wärme-Kopplung

In der Kraft-Wärme-Kopplung (KWK) werden die Feststoffe aus der Fest/Flüssig-Trennung gemeinsam mit dem schwefelfreien Abgas aus der Biogas-Aufbereitung verbrannt. Das heiße Abgas wird zur Erzeugung von Heißdampf herangezogen. Dieser wird in eine Entnahme-Kondensationsturbine geleitet, um elektrischen Strom und Prozessdampf bei zwei Druckniveaus (20 und 4 bar) zu erzeugen. Die Prozessparameter der KWK sind in Tab. 2 aufgelistet.

## 4 Methodik

Massen- und Energiebilanzen wurden mit dem gleichungsorientierten, stationären Fließbildsimulationsprogramm IPSEpro berechnet. Ein Vorteil der für die Simulation von Kraftwerksprozessen entwickelten Software, ist ihre Flexibilität. So konnte die Modell-Bibliothek um Modelle der Ethanol- und Biogasfermentation sowie der Vorbehandlung und Produktaufbereitung erweitert werden [18 – 20].

Um den Einsatz von Prozesswärme zu minimieren wurde eine Pinch-Analyse durchgeführt und ein optimiertes Wärmeübertragernetzwerk berechnet. Dazu wurde eine selbst entwickelte Optimierungssoftware verwendet.

## 5 Ergebnisse und Diskussion

### 5.1 Bilanzen

### 5.1.1 Massenbilanz für Stroh

In Tab. 3 sind die detaillierten Ergebnisse der Massenbilanz für Stroh angegeben. Um 100 000 t Ethanol pro Jahr zu pro-

**Tabelle 3.** Ergebnisse der Massenbilanz für Stroh.

| | $[\mathrm{t\,a^{-1}}]$ |
|---|---|
| *Eingang* | |
| Stroh, feucht (90 % TS) | 648 063 |
| $SO_2$ | 5832 |
| $NH_3$ (28 Gew.-% in $H_2O$) | 12 507 |
| Melasse (80 % TS) | 6621 |
| Corn Steep Liquor (50 % TS) | 19 875 |
| Diammoniumphosphat $(NH_4)_2HPO_4$ | 2500 |
| Phosphorsäure $H_3PO_4$ (100 % Säure) | 438 |
| Prozesswasser Ethanol-Prozess | 2 020 772 |
| Frischwasser für Dampferzeugung | 289 895 |
| Luft (Verbrennung + ARA) | 2 515 141 |
| *Ausgang* | |
| Ethanol (100 %) | 100 000 |
| $BioCH_4$ (98 Vol.-%) | 62 260 |
| Abwasser aus ARA | 2 187 017 |
| Biologischer Schwefel | 1711 |
| $CO_2$ aus Bioreaktoren | 112 977 |
| $CO_2$ aus Abgas | 469 944 |
| $CO_2$ aus ARA | 33 034 |
| Asche nach Verbrennung | 30 082 |
| Schlamm (30 % TS) | 185 273 |
| Schlamm (75 % TS) | 74 109 |

duzieren werden dem Prozess jährlich 648 063 t frisches Stroh (90 % TS) zugeführt. Zusätzlich müssen 5832 t $SO_2$ und 12 507 t $NH_3$ pro Jahr für die Vorbehandlung bereit gestellt werden. Aus der festen Fraktion der Schlempe entstehen nach Trocknung und Verbrennung 469 944 $\mathrm{t\,a^{-1}}$ $CO_2$ und 30 082 $\mathrm{t\,a^{-1}}$ Asche. Für die organischen Substanzen im flüssigen Anteil der Schlempe ergibt sich nach anaerober Fermentation und anschließender Biogas-Aufbereitung ein Biomethan-Ertrag (98 Vol.-% $CH_4$) von 62 260 $\mathrm{t\,a^{-1}}$, dies entspricht $84{,}5 \cdot 10^6\,\mathrm{Nm^3a^{-1}}$. Der Rest der Flüssigfraktion wird in der aeroben Fermentation aufbereitet, wodurch über 2 Mio. Tonnen Wasser jährlich in den Prozess rückgeführt werden. Der dabei entstehende, nährstoffreiche Schlamm kann mit mechanischer Eindickung und solarer Klärschlammtrocknung [21] auf einen Trockensubstanzgehalt von 75 % gebracht werden. Es ergeben sich dadurch 74 109 $\mathrm{t\,a^{-1}}$ (75 % TS) an Schlamm.

### 5.1.2 Massenbilanz für Holz

Die Massenströme für Holz sind in Tab. 4 aufgelistet. Es bedarf 868 599 t an feuchter Fichte (45 % TS) um jährlich 100 000 t EtOH zu produzieren. Die Vorbehandlung erfordert unter anderem 9772 $\mathrm{t\,a^{-1}}$ $SO_2$ und 13 898 $\mathrm{t\,a^{-1}}$ $NH_3$. Aus den Feststoffen der Schlempe ergeben sich in der KWK 7866 $\mathrm{t\,a^{-1}}$ Asche und aus dem flüssigen Teil können 16 491 $\mathrm{t\,a^{-1}}$ Biomethan erzeugt werden. Dies entspricht einem jährlichen Ertrag von $22{,}5 \cdot 10^6\,\mathrm{Nm^3}$. Die Aufbereitung des Wassers nach der anaeroben Fermentation ergibt einerseits 2,1 Mio. $\mathrm{t\,a^{-1}}$ Abwasser zur Rückführung im Prozess und 49 798 $\mathrm{t\,a^{-1}}$ Schlamm (30 % TS), der ebenfalls mittels solarer Klärschlammtrocknung auf 75 % TS gebracht werden kann. Das anfallende biogene $CO_2$ aus dem gesamten Prozess beträgt 493 489 $\mathrm{t\,a^{-1}}$ und gliedert sich in 363 491 $\mathrm{t\,a^{-1}}$ aus der Verbrennung, 112 977 $\mathrm{t\,a^{-1}}$ aus den Bioreaktoren und 17 021 $\mathrm{t\,a^{-1}}$ aus der Abwasser-Aufbereitungsanlage.

**Tabelle 4.** Ergebnisse der Massenbilanz für Holz.

| | $[\mathrm{t\,a^{-1}}]$ |
|---|---|
| *Eingang* | |
| BM feucht (45 % TS) | 868 599 |
| BM trocken | 390 869 |
| $SO_2$ | 9772 |
| $NH_3$ (28 Gew.-% in $H_2O$) | 13 898 |
| Melasse (80 % TS) | 6968 |
| Corn Steep Liquor (50 % TS) | 18 538 |
| Diammoniumphosphat $(NH_4)_2HPO_4$ | 2330 |
| Phosphorsäure $H_3PO_4$ (100 % Säure) | 406 |
| Prozesswasser Ethanol-Prozess | 1 442 863 |
| Frischwasser für Dampferzeugung | 239 279 |
| Luft (Verbrennung + ARA) | 1 926 789 |
| *Ausgang* | |
| Ethanol (100 %) | 100 000 |
| $BioCH_4$ (98 Vol.-%) | 16 491 |
| Abwasser aus ARA | 2 085 814 |
| Biologischer Schwefel | 2684 |
| $CO_2$ aus Bioreaktoren | 112 977 |
| $CO_2$ aus Abgas | 363 491 |
| $CO_2$ aus ARA | 17 021 |
| Asche nach Verbrennung | 7866 |
| Schlamm (30 % TS) Out | 49 798 |
| Schlamm (75 % TS) Out | 19 919 |

### 5.1.3 Vergleich Stroh und Holz

Wenn man nun die Massenbilanzen für die beiden Prozesse vergleicht, so ist zu erkennen, dass für den Aufschluss des Strohs 40 % weniger $SO_2$ benötigt wird (5832 statt

9772 t a$^{-1}$) und dadurch im Biogas-Aufbereitungsschritt weniger biologischer Schwefel entsteht (1711 statt 2684 t a$^{-1}$).

Der größte Unterschied liegt aber im Methanertrag, der für Stroh mehr als 375 % des Ertrags von Holz beträgt (62 260 t a$^{-1}$ zu 16 491 t a$^{-1}$). Mehr Biogas ergibt somit auch mehr Stroh-Schlamm, der ebenfalls im Bereich um die 370 % des Holz-Schlamms liegt. Zudem fällt beim Stroh-Prozess nach der Verbrennung annähernd das 4fache der Holz-Asche an.

## 5.2 Energetische Analyse

Für beide Prozesse ist in den Sankey-Diagrammen (Abb. 2) die Aufteilung der Energieflüsse dargestellt. Als Eingangsgrößen werden der Energieinhalt der Biomasse und der elektrische Prozessbedarf berücksichtigt, woraus sich die drei Hauptprodukte Ethanol, Biomethan und Strom ergeben. Die Hilfsstoffe wurden aufgrund des sehr geringen Beitrags vernachlässigt. Alle nachfolgenden Ergebnisse beziehen sich auf den LHV$_{trocken}$, da sich sonst teilweise negative Ergebnisse ergeben, die in den Sankey-Diagrammen nicht dargestellt werden können. In Klammern sind die zugehörigen Energieinhalte inklusive Wasser (LHV$_{gesamt}$) angegeben.

Die 100 000 t a$^{-1}$ entsprechen bei der angenommen Betriebsdauer von 8000 h a$^{-1}$ einem Wert von 12,5 t h$^{-1}$ (entspricht 3,47 kg s$^{-1}$) was mit dem LHV von Ethanol multipliziert (26 900 kJ kg$^{-1}$) eine Leistung von 93 MW$_{ch}$ ergibt – dies gilt für beide Varianten. Die Eingangsstoffe Stroh und Holz unterscheiden sich sowohl massenmäßig als auch vom Energieinhalt.

### 5.2.1 Stroh-Prozess

Aus einem trockenen Energieinhalt für das eingebrachte Stroh von 365 MW$_{ch}$, ergeben sich die bereits angesprochenen 93 MW$_{ch}$ für das Ethanol, 123 MW$_{ch}$ für die Feststoffe nach der Fest/Flüssig-Trennung und 139 MW$_{ch}$ für die flüssige Schlempe. In der KWK-Anlage werden 25 MW$_{el}$ an Strom erzeugt, 15 MW$_{el}$ davon werden für den Prozessbedarf bereitgestellt und 67 MW$_{th}$ als Heizdampf im Prozess rückgeführt. In der Biogas-Produktion werden aus den 139 MW$_{ch}$, die über die Schlempe zugeführt werden, 103 MW$_{ch}$ als Biomethan wiedergewonnen.

Der Gesamtwirkungsgrad errechnet sich als Quotient der Energie in den Produkten und der Energie im Einsatzstoff (in diesem Fall Stroh). Daraus ergibt sich ein Gesamtwirkungsgrad für den Prozess von 56,4 %, alle bezogen auf den LHV$_{trocken}$.

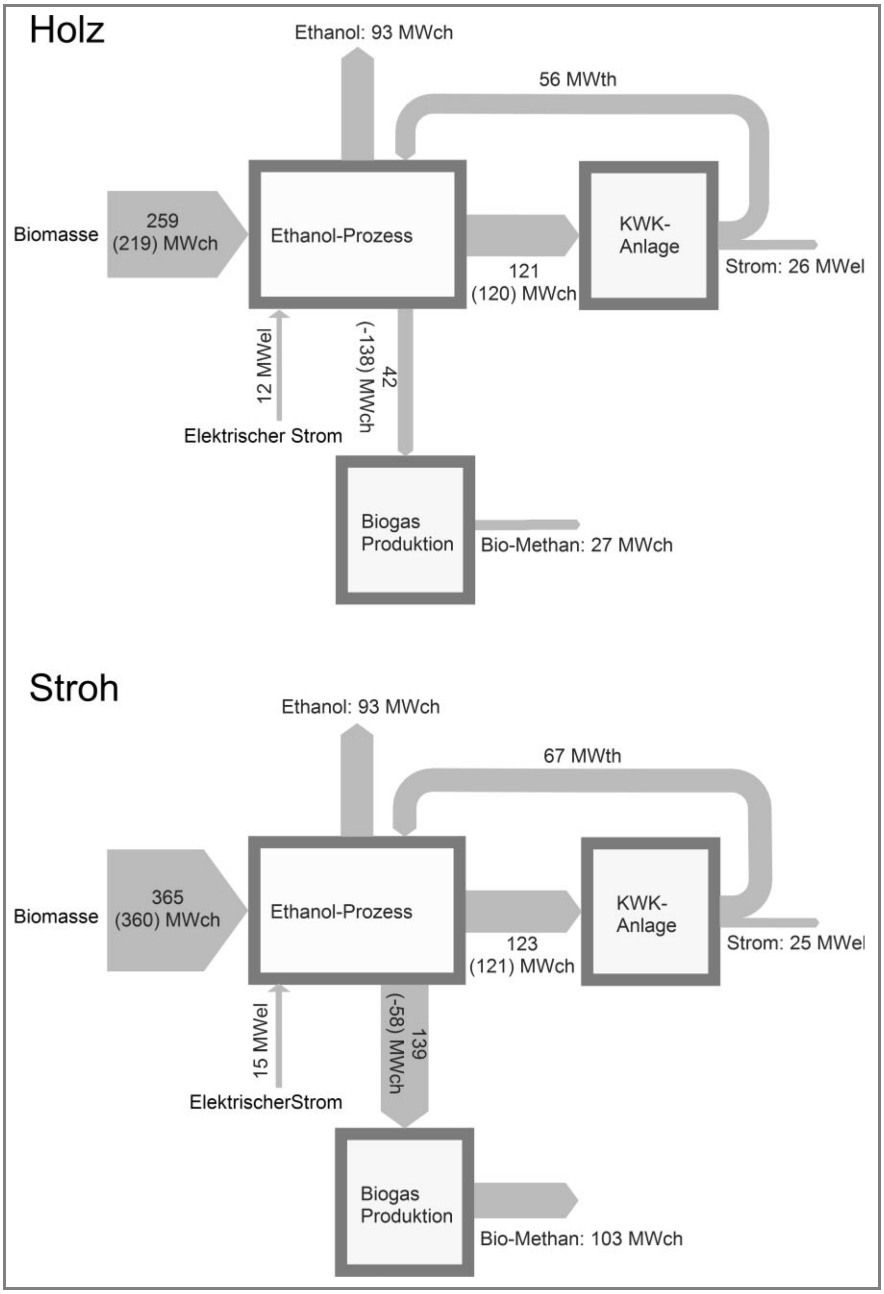

**Abbildung 2.** Sankey-Diagramme für den Holz- bzw. Stroh-Prozess. MW$_{ch}$: chemische Leistung, beschreibt den LHV trocken, MW$_{el}$: elektrische Leistung, MW$_{th}$: thermische Leistung; die in Klammern angeführten Werte beziehen sich auf den LHV gesamt.

### 5.2.2 Holz-Prozess

Das zugeführte Holz hat einen $LHV_{trocken}$ von 259 $WM_{ch}$, woraus sich nach Vorbehandlung, Destillation und Fest/Flüssig-Trennung eine Feststofffraktion mit einem Energieinhalt von 121 $MW_{ch}$ und eine Flüssigfraktion mit 42 $MW_{ch}$ ergeben. In der KWK-Anlage können somit 26 $MW_{el}$ an Strom und 56 $MW_{th}$ an thermischer Energie wieder gewonnen werden, wobei 12 $MW_{el}$ des erzeugten Stroms der Prozessversorgung dienen. Das in der Biogas-Produktion erzeugte Biomethan hat einen Energieinhalt von 27 $MW_{ch}$. Somit lässt sich der Gesamtwirkungsgrad der Anlage zu 52,1 % berechnen.

## 5.3 Technische Aspekte der Biomethan-Produktion aus Schlempe

Aus der energetischen Analyse wird sichtbar, dass sowohl für Stroh als auch für Holz ein sehr großes Potenzial zur Biogasherstellung vorhanden ist. Die größte Problematik bei der Biogaserzeugung liegt in der bereits angesprochenen Abhängigkeit der CSB-Raumbelastung von der Verweilzeit und der daraus resultierenden Fermenter-Größe. Wie in Tab. 2 ersichtlich ist, errechnet sich für Stroh bei einer angenommenen CSB-Raumbelastung von 20 $kg_{CSB}kg^{-1}d^{-1}$, mit einer CSB-Eingangskonzentration von 130 $g\,L^{-1}$ und einer Verweilzeit von 6,5 Tagen ein Reaktorvolumen von 48 800 $m^3$. Für Holz ergibt sich ein Reaktorvolumen von 13 000 $m^3$, wobei die CSB-Konzentration 40 $g\,L^{-1}$ und die Verweilzeit 2,5 Tage betragen. Im Vergleich dazu ist das Reaktorvolumen bei der SSF im Bereich von 20 000 $m^3$. Aus der Massenbilanz ist zu erkennen, dass der Stickstoffgehalt ausreichend für eine gut funktionierende anaerobe Fermentation ist (> 10 $g_N kg_{CSB}^{-1}$), es jedoch notwendig sein wird $H_3PO_4$ zuzugeben um den Mindest-Phosphorgehalt von 1,25 $g_P kg_{CSB}^{-1}$ zu erreichen.

Das Schwefel/CSB-Verhältnis beträgt für Stroh 7 $g_S kg_{CSB}^{-1}$ (s. Tab. 2), somit kann davon ausgegangen werden, dass es zu keiner Sulfid-Inhibition kommt. Holz liegt mit 42 $g_S kg_{CSB}^{-1}$ knapp oberhalb des für die Sulfid-Inhibition kritischen Grenzwerts von 33,3 $g_S kg_{CSB}^{-1}$. Um eine Inhibition gänzlich ausschließen zu können, wäre es wichtig dies experimentell zu überprüfen. Der höhere Wert für Holz hat seine Ursache darin, dass mit 2,5 Gew.-% mehr $SO_2$ in der Vorbehandlung eingesetzt wird. Im Vergleich dazu benötigt man für den Aufschluss von Stroh nur 1 Gew.-% $SO_2$ (bezogen auf die trockene Biomasse). Hier muss noch erwähnt werden, dass für Stroh auch Vorbehandlungstechnologien ohne Einsatz von Säure bekannt sind, was bei Holz undenkbar ist [22].

Auch für das *Upgrading* stellt Schwefel in Form des hohen $H_2S$-Gehalts im Biogas eine Herausforderung dar. So müssen in der Entschwefelung des Stroh-Biogases bzw. Holz-Biogases 99,95 % bzw. 99,99 % des Schwefels abgetrennt werden, um die PSA problemlos betreiben zu können (s. Tab. 2).

Einer der technischen Aspekte, der für die Biogas-Fermentation spricht, ist die Tatsache, dass sich sowohl Asche als auch Stickstoff und Phosphor vorwiegend im Schlamm wiederfinden. Bei einer nicht-thermischen Nutzung des Schlamms ergeben sich dadurch zwei Vorteile. Einerseits kann wertvoller Stickstoff, Phosphor und Mineralien als Nährstoff in die Landwirtschaft zurückgeführt werden. So finden sich ca. 85 % des in den Prozess eingebrachten Stickstoffs und ca. 50 % des in den Prozess eingebrachten Phosphors im Schlamm wieder. Andererseits werden problematische Aschebestandteile nicht der Verbrennung zugeführt. Speziell für Stroh zeichnet sich dies aus, da es mehr Asche bzw. auch mehr Calcium beinhaltet.

## 6 Schlussfolgerung

Die Simulation und Analyse der kombinierten Produktion von Ethanol, Biomethan und elektrischem Strom aus lignocellulosehaltigen Rohstoffen kann als hocheffizienter Prozess beschrieben werden. Sowohl für Holz als auch für Stroh, ergeben sich trotz Bereitstellung der Prozessenergien durch den Rohstoff Wirkungsgrade über 50 %.

Die Bedeutung, die den Prozessen der Produktion von Biogas zukommt wird dadurch verdeutlicht, dass bei beiden Rohstoffen die Schlempe deutlich mehr Energie enthält als das Produkt Ethanol.

Technisch ist die Biogasfermentation der Flüssigfraktion der lignocellulosehaltigen Ethanol-Schlempe jedoch eine Herausforderung. Bei Stroh als Rohstoff ergeben sich trotz der hohen Raumbelastungen Reaktorvolumina, die jene der Ethanolfermentation deutlich übersteigen, was letztendlich die Wirtschaftlichkeit des Prozesses in Frage stellt. Bei Holz als Rohstoff ist der Schwefelgehalt in der Flüssigfraktion die größte Herausforderung. Dieser ist so hoch, dass Sulfid-Inhibition auftreten kann. Besondere Bedeutung kommt der Entschwefelung des Rohbiogases zu. So müssen in den vorliegenden Konzepten sehr hohe Entschwefelungsgrade für einen problemfreien Betrieb erreicht werden.

Nichtsdestotrotz erscheint die kombinierte Produktion von Ethanol, Biomethan und elektrischem Strom als ein attraktives Konzept zur Nutzung von lignocellulosehaltiger Biomasse.

## Abkürzungen

| | |
|---|---|
| ARA | Abwasserrecycling-Anlage |
| CHP | Combined Heat and Power |
| CSB | chemischer Sauerstoffbedarf |
| CSL | Corn Steep Liquor (Maisquellwasser) |
| FPU | Filter Paper Unit |
| ISET | Institut für solare Energieversorgungstechnik |
| KWK | Kraft-Wärme-Kopplung |
| LHV | Lower Heating Value (unterer Heizwert) |

| | |
|---|---|
| PSA | Pressure Swing Adsorption (Druckwechsel-Adsorption) |
| SE | Steam Explosion |
| SSF | Simultaneous Saccharification and Fermentation (gleichzeitige Hydrolyse und Fermentation) |
| TS | Trockensubstanz |
| UASB | Upflow Anaerobic Sludge Blanket (nach dem Gegenstromprinzip arbeitender anaerober Fließbettreaktor) |
| WI | Wärmeintegration |
| YI | Yeast Production (Hefeproduktion) |

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# PAPER V TECHNOLOGY VALIDATION

Kravanja P., Könighofer K., Canella L., Jungmeier G. and Friedl A. (2012)

Perspectives for the production of Bio-ethanol from Wood and Straw in Austria -Technical, economic and ecological aspects.

**Clean technologies and environmental policies** 14(3):411-425

Clean Techn Environ Policy (2012) 14:411–425
DOI 10.1007/s10098-011-0438-1

ORIGINAL PAPER

# Perspectives for the production of bioethanol from wood and straw in Austria: technical, economic, and ecological aspects

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Lorenza Canella · Gerfried Jungmeier ·
Anton Friedl**

**Abstract** Bioethanol produced from lignocellulosic resources is a promising candidate for the replacement of fossil fuels. In this study, we aim to determine the perspectives to produce lignocellulosic ethanol in Austria. Technical, environmental and economic aspects are being considered. Thirteen biotechnological production concepts using the raw materials straw and softwood were established and simulated with the steady state flowsheeting software IPSEpro. Bioethanol production cost and greenhouse gas (GHG) emissions for each system were calculated based on mass and energy balances obtained from process simulation. The emission of GHGs along the entire bioethanol process chain ("from well to wheel") are compared to two reference systems producing the same amounts of by-products. In all concepts, process heat and considerable amounts of the by-products electricity, heat, pellets, C5 molasses, or biomethane could be obtained from residual biomass. Compared to a reference system driven by fossil energy, GHG emissions can be reduced by up to 76%. The production cost of ethanol was found to between 0.66 € and 0.94 € per liter of gasoline equivalent. The type and amount of by-product influence technical, economic, and environmental performance significantly. Converting all straw and softwood available in Austria to ethanol would result in an annual production of 340 kt.

**Keywords** Bioethanol · Lignocellulosic resources · Energy balance · Greenhouse gases (GHG) · Life cycle assessment (LCA) · Economic evaluation

## Abbreviations

| | |
|---|---|
| CSL | Corn steep liquor |
| DAP | Diammoniumphosphate $(NH_4)_2HPO_4$ |
| DM | Dry matter |
| GHG | Greenhouse gas |
| LCA | Life cycle assessment |
| LHV | Lower heating value |
| SSF | Simultaneous saccharification and fermentation |
| WIS | Water insoluble solids |

## Introduction

Today fuel ethanol produced from lignocellulosic materials is on the brink of commercialization. This situation is a result of great research efforts made in the past decade and owes to high expectations in this fuel, which are also reflected in policies in both, the EU and the United States of America (European Union 2009a, b; US EPA 2009). Various appealing features of the fuel and technology form the basis of the great interest.

Ethanol from lignocellulosic biomass is a renewable fuel and can be produced from local resources. Hence, it is an attractive substitute for fossil fuels reducing depletion of shrinking oil resources as well as dependence of oil imports and thereby helping to secure the energy supply of the future. Also from a purely technical standpoint, ethanol is suited to complement or replace gasoline. Fuel ethanol has very good combustion properties and when blended with conventional gasoline at low concentrations (E5), it can be

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used in standard Otto engines using the existing infrastructure. However, when ethanol is used at higher concentrations or in pure form slight modifications of engine and infrastructure become necessary (Balat and Balat 2009). Moreover, the food versus fuel debate can be tackled by lignocellulosic ethanol. Compared to bioethanol from conventional crops lignocellulosic ethanol can be produced using residual materials from feed and food production. Thereby, allocation of additional land for biofuel production can be avoided. Ultimately lignocellulosic ethanol is a potential low carbon fuel that can contribute to reach climate change goals, which is not true for all biofuels. While for bioethanol from corn and wheat, many factors decide whether it is a good or bad biofuel (Boerjesson 2009), there is a broad consensus that ethanol from lignocellulosic biomass mitigates greenhouse gas (GHG) emissions. Von Blottnitz and Curran (2007) reviewed 47 scientific publications dealing with GHG emissions of bioethanol systems and found emission reductions for all types of lignocellulosic materials. According to Eisentraut (2010), who summarized well to wheel GHG emission changes of various biofuels compared to fossil fuels, reductions ranging from 60 to 110% for lignocellulosic ethanol can be achieved. Slade et al. (2009) examined GHG emissions of cellulosic ethanol supply chains in Europe. In the base case scenarios, reductions between 56 and 82% were attained. However, to actually achieve these promising results, employment of waste biomass or biomass from degraded land is necessary (Fargione et al. 2008; Slade et al. 2009; Balat and Balat 2009, 2010).

The technical challenges for producing lignocellulosic ethanol commercially are inherent to the feedstock. Compared to conventional crops for ethanol production the sugar content is lower and the carbohydrates are harder to access (Banerjee et al. 2010). These features of the feedstock translate to increased investment and energy cost. As recent discussions in Germany showed (Handelsblatt Online 2011), lacking acceptance of consumers and industry can also inhibit the introduction of bioethanol. Nonetheless, we think that once the technology is proven on a commercial scale, lignocellulosic ethanol will contribute to reduce our dependence on fossil fuels.

### Bioethanol and biomass in Austria

By EU legislation, renewable energy in the transport sector has to reach a share of 10% (European Union 2009a, b) by 31 December 2020. Until the same date, fuel suppliers are required to reduce life cycle GHG emissions by 6% (European Union 2009a). These goals can only be reached by means of biofuels. At present, biofuels are prescribed to account for 5.75% of fuels in Austria, based on energy (European Union 2003). This share has been successfully implemented via blending of diesel with biodiesel and gasoline with bioethanol, respectively. As far as ethanol is concerned, there is one starch based facility in Pischelsdorf, Lower Austria whose capacity is 191 kt/year and suffices to supply the ethanol necessary to reach the 5.75% target. However, assuming stagnant gasoline consumption in Austria a 10% energy share of bioethanol in gasoline cannot be reached with the current production capacity (Winter et al. 2010). As a consequence, new resources for bioethanol production have to be tapped.

As far as lignocellulosic resources for bioethanol production are concerned, straw (both maize and wheat straw) and softwood (spruce) have the largest potential in Austria. Based on grain yields and typical grain/straw ratios, the sum of wheat straw and maize straw available for energy recovery was estimated to be 950 kt/year in 2008 (Statistik Austria 2011b). In this context, we assumed, that 20% of straw are available for energy recovery. As for spruce, in 2006, the amount available for production of biofuels was estimated at 750 kt dry matter (DM) (BMLFUW 2006). Here it is important to note that, in Austria, it is not planned to provide additional land for biofuel production. Hence, the biomass potentials indicated here do include only biomass resources presently available in Austria. This limitation justifies that no land use change issues are addressed in this study.

### Goal of this study

In this article, Austrian perspectives for the production of ethanol from lignocellulosic biomass are discussed. For that purpose, thirteen biotechnological production concepts were established. Energy self sufficiency is a prerequisite for all the concepts and can be achieved by burning part of the residual materials. Residual materials exceeding the process heat demand are used for by-product generation. By-products are characteristic of the respective concept and can substantially improve process performance. Production concepts are analyzed on technical, economic, and ecologic performance using process simulation, cost comparison method, and life cycle assessment (LCA), respectively.

## Methodology

The most promising production concepts for lignocellulosic ethanol production were established after a thorough analysis (Kravanja and Friedl 2010) of the scientific literature and worldwide demo plants (IEA Bioenergy Task 2011). The analysis revealed that steam explosion and simultaneous saccharification and fermentation (SSF) are at present the most widespread and developed process technologies. Consequently all concepts considered in this study are based on these technologies. Biomass potentials in Austria were taken into account for selection of the raw materials straw and softwood. Mass and energy balances were computed by means of process simulation. The data thus obtained was used for calculation of GHG emissions of the entire bioenergy system, which includes all steps of the process chain ("from cradle to grave"). Moreover, concepts were analyzed on economic performance by comparison of ethanol production cost.

## Production concepts

Detailed mass and energy balances including all auxiliary and waste materials were computed using the equation oriented, steady state flow sheeting software IPSEpro. A model library containing the necessary unit operations and capable of handling the complex materials present in a lignocelluloses to ethanol process was constructed (Schausberger et al. 2010) and is improved and augmented continuously. Pinch analysis and heat exchanger network synthesis were carried out using in-house optimization software based of Wolfram Mathematica. Heating values of the biomass streams were calculated by applying the PLS model of Friedl et al. (2005) to elementary compositions obtained from mass balances.

What follows is a technical description of the 13 biotechnological production concepts simulated with IPSEpro. Two types of biomass, straw and softwood are considered. Straw has 90% DM, containing 39 w/w% hexosan, and 23 w/w% pentosan (Lee et al. 2007). Softwood composition with 45% DM containing 58 w/w% hexosan and 8 w/w% pentosan was obtained by an analysis of various sources including Sassner et al. (2008) and Zhu and Pan (2010). The production concepts examined in this work are listed in Table 1 and differ in type of biomass, utilization of sugars in SSF, allocation of electricity, and by-products obtained from the stillage.

In all concepts, process heat is supplied by burning part of the stillage leaving distillation. Hence, no fossil fuels are employed in the conversion process. In order to minimize process heat demand and thereby maximize by-product output, heat integration is applied. Since opportunities for heat recovery depend on flowsheet setup, conversion rates, and process conditions six different heat exchanger networks (A–F) were implemented, as shown in Table 1.

Figure 1 shows a simplified summary of the enumerated concepts including all material flows crossing the system boundary of the production process. As can be seen all concepts but one (concept 8) are identical regarding type and configuration of the upstream process, SSF and product recovery section. Concept 8 resembles INBICON's IBUS process (Larsen et al. 2008) and includes an additional solid–liquid separation and washing step in the upstream part of the process. As a consequence, SSF can be performed at higher water insoluble solids (WIS) content (high WIS in Table 1).

**Table 1** Summary of concepts investigated

| No. | Biomass | Fermentation | Allocation of electricity | By-products from stillage | | Heat exchanger network |
|---|---|---|---|---|---|---|
| 1 | Straw | C6 | produced on-site | Electricity | | A |
| 2 | Straw | C6+C5 | produced on-site | Electricity | | B |
| 3 | Straw | C6 | produced on-site | Electricity | Heat | A |
| 4 | Straw | C6 | purchased | Pellets | | A |
| 5 | Straw | C6+C5 | purchased | Pellets | | B |
| 6 | Straw | C6 | purchased | Pellets | Heat | A |
| 7 | Straw | C6 | purchased | C5 Molasses | Pellets | A |
| 8 | Straw | C6, high WIS | purchased | C5 Molasses | Pellets | C |
| 9 | Straw | C6 | purchased | C5 Molasses | Heat | A |
| 10 | Straw | C6 | produced on-site | Biomethane | Electricity | D |
| 11 | Softwood | C6 | produced on-site | Electricity | | E |
| 12 | Softwood | C6 | purchased | Pellets | | E |
| 13 | Softwood | C6 | produced on-site | Biomethane | Electricity | F |

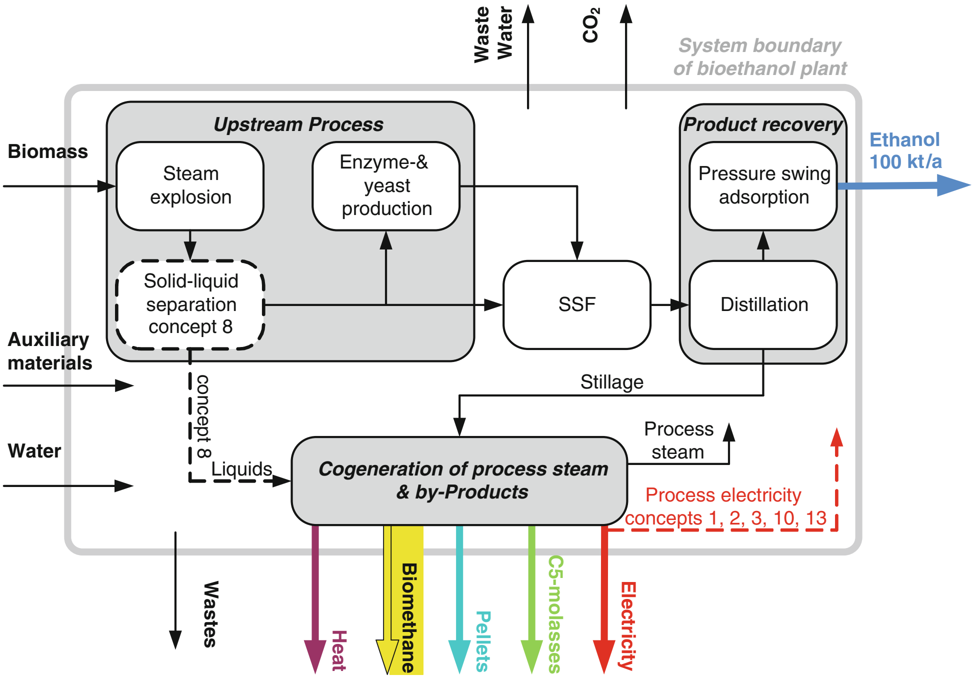


**Fig. 1** Scheme summarizing the 13 concepts. *SSF* simultaneous saccharification and fermentation. *Solid black lines* Included in all concepts. *Dashed lines within boundary* Only enumerated concepts. Supplies include: $SO_2$ (sulfur dioxide) and $NH_3$ (ammonia) for steam explosion and neutralization, CSL, DAP, beet molasses, and $H_3PO_4$ (phosphoric acid, only concepts 10 and 13). Waste materials include ash from combustion and sludge from anaerobic digestion and AWT

In all concepts, 100 kt ethanol are produced annually. Operating time is assumed to be 8,000 h/year. Model assumptions and conversion rates of reactions were obtained from a detailed review of the literature and are elsewhere summarized more extensively (Kravanja and Friedl 2011; Lassmann et al. 2011).

## Upstream process, SSF, and product recovery

Fresh biomass is reduced in size, preheated, and fed to steam explosion, which is performed under addition of small amounts of $SO_2$. Straw has to be moistened prior to steam explosion whereas fresh softwood has higher moisture and does not require addition of water. In steam, explosion parts of hexosan and pentosan are dissolved, a small fraction is lost due to degradation. Because of the higher yields wood is subjected to two-step pretreatment (Monavari et al. 2009), whereas for straw conventional one step pretreatment is assumed. As suggested by Wingren et al. (2003) flash steam is recovered at two pressure levels and used for indirect heating elsewhere in the process and subsequently disposed of.

The hot, steam exploded biomass is cooled, neutralized with $NH_3$, and thereafter in all concepts but one (8), split into three streams. Minor fractions are used for on-site enzyme production and yeast propagation whereas the major part is directly fed to SSF. In concept 8, steam exploded straw is subjected to a solid–liquid separation and washing step. Dissolved sugars and degradation products are mainly recovered in the liquid fraction which is sent to the cogeneration section after a small amount was removed for yeast propagation. Solids are used for enzyme production and SSF, which can be performed at 20% WIS, thereby reducing investment and operating cost. However, separation and washing causes loss of sugars dissolved in steam explosion and consequently reduces ethanol yield.

In all concepts, yeast propagation is performed with pretreated biomass enhanced with beet molasses, whereas pretreated biomass is the sole carbon source for enzyme production. Anyway, less than 5% of biomass is used for enzyme production assuming yields and activities achieved with standard substrates (Lynd et al. 2002; Esterbauer et al. 1991). In concepts without solid–liquid separation after steam explosion (1–7, 9–13), SSF is performed at 12 and 10% WIS for straw and wood, respectively. Cellulose to glucose and glucose to ethanol conversion are both assumed to be 92% in all concepts. Industrial fermentation of C5 sugars to ethanol requires genetically modified organisms (Hahn-Haegerdahl et al. 2007) and is consequently at present not an option in Austria. Therefore, C5 fermentation is considered in only two cases (concepts 2 and 5) for comparison and evaluation of future options. In these concepts C5 sugar to ethanol conversion is assumed to be 75%. For all concepts the specific enzyme loading is 15 Filter paper units per gram of Cellulose. In all bioreactors (yeast propagation, enzyme production, SSF) corn steep liquor (CSL) and diammoniumphosphate $(NH_4)_2HPO_4$ (DAP) are added to meet the respective nutrient requirements.

The beer from SSF contains 4–6 w/w% ethanol, depending on the concept. Highest ethanol concentrations are achieved with C5 fermentation and increased WIS content (concepts 2, 5, and 8). Ethanol is recovered using two parallel stripper columns and one rectifier column as suggested by Sassner et al. (2008). The head product from the rectifier is compressed, superheated and sent to a pressure swing adsorption system (PSA), where a 99.5 w/w% ethanol product is obtained. 25% of that product are used for regeneration of the loaded bed and thereafter returned to the rectifier. The remaining product is condensed and cooled and ready for use as a fuel.

### Cogeneration of process steam and by-products

In all concepts, process residues are used for the cogeneration of by-products (see Table 1) and process heat. When electricity is produced on-site (concepts 1–3, 10, 11, 13), part of the electricity is used to cover the process demand. For these concepts, the conversion process is entirely energy self sufficient. Electricity exceeding the process demand can be sold to the grid as a by-product. For the remaining concepts (4–9, 12), electricity for process needs has to be purchased from the grid. In concepts using straw, residual ash produced by incineration of the residues can partly be returned to farming land and replace mineral fertilizer (Kaltschmitt et al. 2009), whereas fly ash has to be land filled. In softwood concepts, all ash is land filled.

The first step of the cogeneration section is the separation of insoluble solids from water and soluble solids, assuming a DM content of 45% of the solid fraction and 99% recovery of insoluble solids. No washing is considered. As suggested by Sassner et al. (2008), solids are dried by means of a superheated steam dryer operating at 4 bar. Final DM content is assumed to be 90%. Secondary steam obtained from the dryer is used for indirect heating elsewhere in the process and subsequently disposed of. The liquid fraction containing a large share of soluble solids is either sent to an evaporation train (concepts 1–9, 11, 12), as proposed by Aden et al. (2002) or Wingren et al. (2003, 2008), or to an anaerobic digestor (concepts 10 and 13), as proposed by Wingren et al. (2008) and Barta et al. (2010).

#### *By-product electricity (concepts 1, 2, 3, 11)*

This concept is examined for straw (1, 2, 3) and for softwood (11). It is examined in combination with fermentation of C6 sugars only (1, 3, 11) as well as fermentation of C6 and C5 sugars (2). The liquid fraction is evaporated in a five effect, co-current evaporation train. The final DM content of the concentrate is assumed to be 50%. Condensed vapors from the evaporation train can partly be recycled to the process (Larsson et al. 1997), the rest is disposed of. All dried solids and the entire concentrate from evaporation are burnt at 820°C. In concepts 1, 2, and 11, hot flue gases are used to generate primary steam at 650°C and 65 bar. The steam drives a condensing turbine with two extraction ports. Electricity is produced and steam required for the process is extracted (Aden et al. 2002; Sassner and Zacchi 2008). Steam, which is not extracted for process needs, is condensed at 50°C using cooling water.

In concept 3, steam is produced at 700°C and 65 bar and the portion, which is not extracted is condensed at 120°C. The heat of condensation is used to raise the temperature of hot cooling water of the process to the supply temperature of a district heating grid. Supply and return temperature are assumed to be 110 and 50°C, respectively.

The isentropic efficiency of the turbine and the electrical efficiency of the generator are always set to 87 and 97%, respectively.

#### *By-product pellets (concepts 4, 5, 6, 12)*

This concept is considered for softwood (12) and for straw (4, 5, 6). In case of straw fermentation of C6 sugars only (4, 6) as well as fermentation of C6 and C5 sugars (5) are examined. Electricity is purchased from the grid. Evaporation and drying are identical to the concepts described above (see Sect. "By-product electricity (Concepts 1, 2, 3, 11)"). However, instead of burning all the materials originating from drying and evaporation, only the amount required to meet the process heat demand is incinerated and employed to generate saturated process steam at 20 and 4 bar. Excess materials are pelletized, sold as a solid fuel and can be co-fired in an existing power plant. Simulations showed, that for straw and C6 fermentation (4 and 6), the energy content of the concentrated soluble solids from evaporation is more than sufficient to meet the process heat demand. Consequently there are two options to utilize the amount exceeding the process heat demand. In concept 4, the excess amount of the concentrate is dried together with insoluble solids and pelletized. In concept 6, all of the concentrated soluble solids are incinerated and steam exceeding the process demand is used to raise the temperature of hot cooling water of the process to the supply temperature of a district heating grid (see Sect. "By-product electricity (Concepts 1, 2, 3, 11)").

#### *By-products C5 molasses (concepts 7, 8, 9)*

This concept is investigated for straw in combination with fermentation of C6 sugars. In concept 7 and 9, SSF is performed at 12% WIS, whereas in concept 8 inhibitory compounds were removed after steam explosion and SSF can be performed at 20% WIS (see Sect. "Upstream process, SSF and product recovery"). In these concepts, the liquid fraction is evaporated to a DM content of 65% and sold as a product containing mainly C5 sugars. According to Larsen et al. (2008), the so-called C5 molasses are well suited as an animal feed for pigs and cows.

Insoluble solids are dried, as described above (see Sect. "By-product electricity (Concepts 1, 2, 3, 11)") and the amount necessary to meet the process demand is incinerated. In concepts 7 and 8, insoluble solids exceeding the process heat demand are pelletized and sold as a solid fuel, whereas in concept 9 all of the insoluble solids are incinerated and steam exceeding the process demand is used to raise the temperature of hot cooling water of the process to the supply temperature of a district heating grid (see Sect. "By-product electricity (Concepts 1, 2, 3, 11)").

### *By-product biomethane (10, 13)*

This concept is examined for straw (10) and wood (13). Insoluble solids are dried and incinerated to produce electricity and process steam as described above (see Sect. "By-product electricity (Concepts 1, 2, 3, 11)"). Soluble solids, however, are not sent to evaporation but to an anaerobic digestion facility (AD), where organic compounds are decomposed and biogas is formed. It is assumed, that 75% of the chemical oxygen demand (COD) are converted to biogas, containing mainly $CH_4$ and $CO_2$, whereas 15% of the COD are converted to anaerobic sludge. The raw biogas is desulfurized biologically and dried. Thereafter $CO_2$ is separated from $CH_4$ using PSA technology. It is assumed that 3% of $CH_4$ are lost in the waste gas, which is combusted together with insoluble solids. The product gas contains 98 v/v% of methane and can be injected to the natural gas grid or used to supply a filling station for natural gas vehicles. The wastewater from the AD is sent to an aerobic water treatment stage (AWT), where the remaining 10% of COD fed to the AD are converted to $CO_2$, water and aerobic sludge. Water leaving the AWT can be recycled to the process unrestrictedly. Sludge produced in the AD and AWT is concentrated mechanically (thickened) and can be recycled to farming land to replace mineral fertilizer (VCH 1997). A more detailed description of the combined production of ethanol, biomethane and electricity can be found elsewhere (Lassmann et al. 2011).

## GHG assessment

To determine the life cycle-based GHG emissions of the production concepts described in Sect. Production concepts, the software tool GEMIS Version 4.5 (GEMIS 2011) was used. Carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) emissions are calculated for the whole bioethanol process chain as well as for two reference process chains providing the same amount of services. Total GHG emissions are calculated as carbon dioxide equivalents ($CO_2$eq), and reported in kilotons $CO_2$eq per year. Life cycle inventory data is obtained from prior projects (Haas et al. 2008, 2009) or included in the GEMIS database (GEMIS 2011).

### Bioethanol process chain

In LCA, GHG emissions from all stages of the bioethanol process chain including combustion of ethanol in the engine (fuel cycle) as well as the manufacture of the car (vehicle cycle) are considered. The so formed bioethanol system includes:

- Production, collection, and transport of raw materials.
- Bioethanol production plant and operating materials (described in detail in Sect. "plant and operating materials").
- Bioethanol distribution and use in vehicles.
- Construction of the vehicle.
- Use of by-products.
- Disposal or use of wastes.

As far as raw material production is concerned, there is a significant difference between straw and softwood. In softwood production no fertilizer has to be applied (Slade et al. 2009), whereas the nutrients N, P, and K removed from the field in the form of straw have to be replaced by mineral fertilizer. Key assumptions regarding raw material harvest and transport are summarized in Table 4. The harvested biomass is transported to the ethanol production facility by 14 t trucks. The lower density of straw results in higher transport distances, which was accounted for. Transport distances in Table 4 include the trip from the point of harvest to the conversion plant and back. Hence, biomass is harvested within a radius of a little less than 50 and 100 km around the plant for wood and straw, respectively.

GHG emissions associated with the bioethanol production plant include (i) emissions from construction materials, erection and disposal of the plant, (ii) emissions associated with the manufacture and transport of auxiliary materials, (iii) emissions associated with waste water treatment, (iv) emissions from combustion of residual biomass, and (v) in the concepts where electricity is purchased from the grid the emissions from electricity production. As far as ethanol plant emissions from fermentation and combustion of residual biomass are concerned $CO_2$ emissions are not counted as GHG emissions. However, typical $CH_4$ and $N_2O$ emissions of biomass combustion systems are considered (see Table 2). The neutrality of $CO_2$ emissions is this section of the chain is due to sequestration of $CO_2$ during plant growth and assumes sustainable wood and straw production in Austria. Since biomass potentials described above only consider residual biomass already available in Austria this assumption is justified.

**Table 2** Data used in life cycle analysis

| Energy use in biomass production and transport | Straw | Softwood | | |
|---|---|---|---|---|
| Harvesting consumption (l diesel/t fresh biomass) | 3.29 | 7.80 | | |
| Transport distance (km) | 200 | 100 | | |
| Fuel consumption truck (l diesel/100 km) | 16.09 | 16.09 | | |
| Truck payload (t) | 14 | 14 | | |
| Emissions from biomass production | $CO_2$ | $CH_4$ | $N_2O$ | $CO_2$eq |
| Production N fertilizer (g/kg) | 1730 | 3.30 | 12.03 | 5399 |
| Production $P_2O_5$ fertilizer (g/kg) | 3787 | 12.23 | 0.14 | 4134 |
| Production $K_2O$ fertilizer (g/kg) | 75.52 | 0.18 | 0.002 | 80.56 |
| Field emissions N fertilizer (g/kg) | | | 16.34 | 4870 |
| Emissions from ethanol plant | | | | |
| Residual biomass combustion (g/$MWh_{input}$) | 0 | 9.73 | 19.50 | 6054 |
| Emissions from ethanol use | | | | |
| Production of ethanol vehicle (g/km) | 18.20 | 0.07 | 0.001 | 20 |
| Direct emissions from ethanol combustion (g/km) | 0 | 0.004 | 0.001 | 0.42 |

For bioethanol distribution, 28 t trucks and a driving distance of 250 km are assumed (Haas et al. 2009). Ethanol use in internal combustion engines is considered neutral regarding $CO_2$ emissions due to sustainable biomass production in Austria. However, $CH_4$ and $N_2O$ emissions from ethanol combustion are considered as well as emissions associated with construction and disposal of the ethanol vehicle (see Table 2).

Emissions from the use of by-products are considered to be GHG neutral except for transport emissions and emissions from combustion of biomethane (concepts 10 and 13).

Ash produced during the combustion of residual biomass is the major waste produced. In the cases of straw ash, heavy metal content was obtained from mass balances and found to be well below limits of ash fertilizers (Kaltschmitt et al. 2009). Nonetheless, we assumed that fly ash, which is typically higher in heavy metals than coarse ash has to be land filled, whereas coarse ash can be used to replace mineral fertilizer. In this context we assumed that fly ash accounts for 10% of total ash, a typical value for biomass combustion (Kaltschmitt et al. 2009), and that all of the coarse ash (90% of total ash) can be used to replace mineral fertilizer. It must be noted that ash does not contain N and hence only P and K fertilizer can be replaced by ash. Since softwood does not require fertilization softwood ash is not used to replace fertilizer and all ash in land filled. Emissions for transport of ash to the field and the land fill are included in the analysis.

## Reference systems

The environmental impact of the bioethanol systems is compared to two types of reference systems. The energy and by-product output of each reference system is identical to the output of the corresponding bioethanol system. Allocation of by-product emissions is thus performed by expanding the reference system to yield the same amount of services, which is one of several options for by-product allocation (Boerjesson 2009). Hence, no emission credits for by-products are given. As for the bioethanol systems GHG emissions of the reference systems were calculated on a life cycle basis including all emissions associated with raw material extraction, transport, refinement and use. Life cycle data for the reference systems was obtained from prior projects (Haas et al. 2008, 2009).

**Table 3** By-product generation in the two types of reference systems

| By-product | Fossil reference | Renewable reference |
|---|---|---|
| Electricity | Natural gas fired power plant | Biomass (co-)fired power plant |
| Electricity + heat | Natural gas fired CHP plant | Biomass fired CHP plant |
| Pellets | Natural gas fired heating station | Biomass fired heating station |
| C5 molasses | Soybeans | Soybeans |
| Biomethane | Natural gas | Natural gas |

In the first type of reference systems, gasoline is used in vehicles and fossil resources are employed for generation of by-products. For example, the by-products electricity and heat are generated from a gas fired combined heat and power plant. This type of reference systems is henceforward referred to as “fossil reference”. In the second type of reference systems, electricity and heat are produced from renewable energy (straw or wood). Thereby the sole effect of replacing gasoline with lignocellulosic ethanol is shown. This type of reference systems are henceforward referred to as “renewable reference”. Table 3 shows how by-products are generated in the reference systems.

**Table 4** Combined mass and energy balances of the 13 production concepts

| **No.** | **Biomass** | | **Conversion** | **Product** | **By-products** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Type | Mass | SSF | Ethanol | Heat | Electricity | C5 Molasses (dry) | Pellets (dry) | Bio-methane |
| | | kt/y | | | GWh/y | GWh/y | kt/y | kt/y | GWh/y |
| 1 | **Straw** | 648 | C6 | **100 kt/y**<br>**747 GWh/y** | | **379** | | | |
| 2 | | 446 | C5+C6 | | | **160** | | | |
| 3 | | 648 | C6 | | **1003** | **305** | | | |
| 4 | | 648 | C6 | | | | | **246** | |
| 5 | | 446 | C5+C6 | | | | | **117** | |
| 6 | | 648 | C6 | | **580** | | | **191** | |
| 7 | | 648 | C6 | | | | **192** | **56** | |
| 8 | | 695 | C6, High WIS | | | | **217** | **90** | |
| 9 | | 648 | C6 | | **551** | | **192** | | |
| 10 | | 648 | C6 | | | **78** | | | **822** |
| 11 | **Soft-wood** | 869 | C6 | | | **176** | | | |
| 12 | | 869 | C6 | | | | | **114** | |
| 13 | | 869 | C6 | | | **114** | | | **219** |

In all concepts, 100 kt of ethanol corresponding to 747 GWh of fuel power are produced

### Economic evaluation

To evaluate the economic performance of the production concepts, static cost comparison method using annual costs and revenues is employed. We assumed an interest rate of 5% and depreciation time of 15 years. Costs comprise:

- Capital costs (annual investment costs, annual interest rate on investment).
- Fixed operating costs (service and maintenance, insurance).
- Variable operating costs (raw material, personal, auxiliary materials, water, waste water treatment, and energy).

To determine investment costs, the production plants were divided into the sections (i) bioethanol production (ii) CHP production (iii) biogas production, and (iv) pellet production. The costs for each section were calculated based on mass flow or energy flow. Cost data for each section was obtained from a prior project (Jungmeier et al. 2007).

Revenues are obtained from the sale of by-products. The difference between annual costs and revenues is ascribed to bioethanol production costs. Specific costs of bioethanol are calculated on energy base (MJ or gasoline equivalent) and yearly production base (L).

Raw material costs, investment costs, and revenues from by-products are still uncertain and largely influence bioethanol production costs. Thus, sensitivity analysis on bioethanol production cost was carried out, for these factors.

## Results

In the following mass and energy balances, GHG emissions and results of economic evaluation are reported. In the case of GHG emissions and cost analysis, detailed results are shown for one example and summaries for all the concepts.

### Mass and energy balances

Combined mass and energy balances of the 13 production concepts are summarized in Table 4. In concepts, where only C6 sugars are fermented to ethanol and no solid–liquid separation is performed upstream, approx. 648 kt (2,877 GWh) of straw with 90% DM or 869 kt (1,750 GWh) of softwood with 45% DM have to be employed to produce 100 kt (747 GWh) of ethanol. Both values correspond to a process yield of approximately 78% of theory, based on C6 sugars and 26 and 43% of energy in the raw material recovered in the ethanol product, respectively. The higher fraction of energy recovered in the case of softwood is due to the higher content of C6 sugars and the higher water content, the latter translating to a smaller lower heating value (LHV) of the raw material. When the liquid fraction is removed after steam explosion (concept 8) sugar losses reduce the process yield to 73% of theory, corresponding to 695 kt (3,086 GWh) of straw. Assuming that C5 sugars are also fermented to ethanol (concepts 2 and 5) the amount of straw required can be reduced to 446 kt (1,983 GWh).

In spite of the fact that a part of the residual materials is burnt to generate process heat, considerable amounts of by-products are obtained in all concepts (see Table 4). This is particularly true for district heat, where the by-product exceeds the main product ethanol on energy basis. However, concepts where district heat is produced are locally restricted to areas, where the large supply meets corresponding demand. In concepts where electricity is obtained as a by-product (1–3, 10, 11, 13) only the amount exceeding the process demand is listed as a product, which can be sold to the grid. C5 molasses, listed in terms of mass, can be used for animal nutrition. To assess the nutritional value of C5 molasses, nitrogen content is derived from mass balances showing that the Nitrogen content of C5 molasses corresponds to approximately 65% of the Nitrogen content of soybeans (GEMIS 2011). Hence 1 kg of C5 molasses is set to replace 0.65 kg of soybeans in LCA and economic evaluation. Pellets, here also listed in terms of mass, can be co-fired in power plants. The LHV of pellets was derived from elementary composition and depending on the concept amounts to 4.6–5.4 kWh/kg at 90% DM. Biomethane can also be obtained in large quantities, especially when straw is used as feedstock. This is mainly due to the high content of C5 sugars, which are not fermented to ethanol in the respective scenario.

Mass balances for auxiliary and waste materials are shown in Table 5. Due to its recalcitrance softwood requires more severe conditions in the pretreatment. Consequently in the concepts employing softwood (11–13) maximum values for $SO_2$ and $NH_3$ are reached. Values for nutrients (Molasses, CSL and DAP) do not differ substantially among the concepts. $H_3PO_4$ is only employed in concepts with an AD and AWT (10 and 13), however, the amounts necessary are small compared to other auxiliary materials. Large quantities of ash are produced. The highest values are reached for concepts (1–3), where straw with its high ash content is used and all residual materials are burnt on-site. When pellets or C5 molasses are produced, part of the ash leaves the system with these products and is not accounted for in Table 5.

## Life cycle assessment

LCA was conducted for each bioethanol system, as well as for two respective reference systems providing the same amount of energy and by-products. GHG emissions of the bioethanol systems and the respective reference systems were calculated in carbon dioxide equivalents ($CO_2$eq).

In Fig. 2, the process chain for one selected bioethanol production system and the respective fossil reference system is shown. As described in Sect. "Greenhouse gas assessment", both systems produce the same amount of energy services, in this case (concept 1) fuel for transportation and electricity. In the bioethanol system, all services are produced from straw whereas in the fossil reference system transport fuel and electricity are produced from oil and natural gas, respectively. In the renewable reference system (not shown in Fig. 2), ethanol is replaced with gasoline produced from oil whereas by-products are produced from straw. When the renewable reference system is used it is assumed, that by-products obtained from bioethanol production do not replace fossil energy, whereby the sole effect of replacing gasoline with lignocellulosic ethanol is shown. In Austria, still large quantities of the potential by-products are produced from fossil energy, hence at present the Austrian situation is reflected in the fossil reference system. As described in Sect. "Bioethanol process chain", nutrients removed from the soil by the withdrawal of straw are replaced by mineral fertilizer and ash. In the fossil reference system, straw is plowed in and no fertilizer has to be applied.

**Table 5** Range of mass flows of auxiliary (A) and waste materials (W) among production concepts

| A/W | Material | Minimum (kt/year) | Maximum (kt/year) | Concepts maximum | Concepts minimum |
|---|---|---|---|---|---|
| A | A, $SO_2$ | 4 | 10 | 2, 5 | 11, 12, 13 |
| A | A, $NH_3$ (28% DM) | 12.5 | 14 | 2, 5 | 11, 12, 13 |
| A | A, beet molasses (80% DM) | 6.6 | 7 | 2, 5 | 11, 12, 13 |
| A | A, CSL (50% DM) | 16.6 | 20 | 2, 5 | 8 |
| A | A, $(NH_4)_2HPO_4$ (DAP) | 2.3 | 2.5 | 2, 5 | 8 |
| A | A, $H_3PO_4$ | 0.4 | 0.44 | 13 | 10 |
| W | W, ash | 15.2 | 51.8 | 1, 3 | 12 |

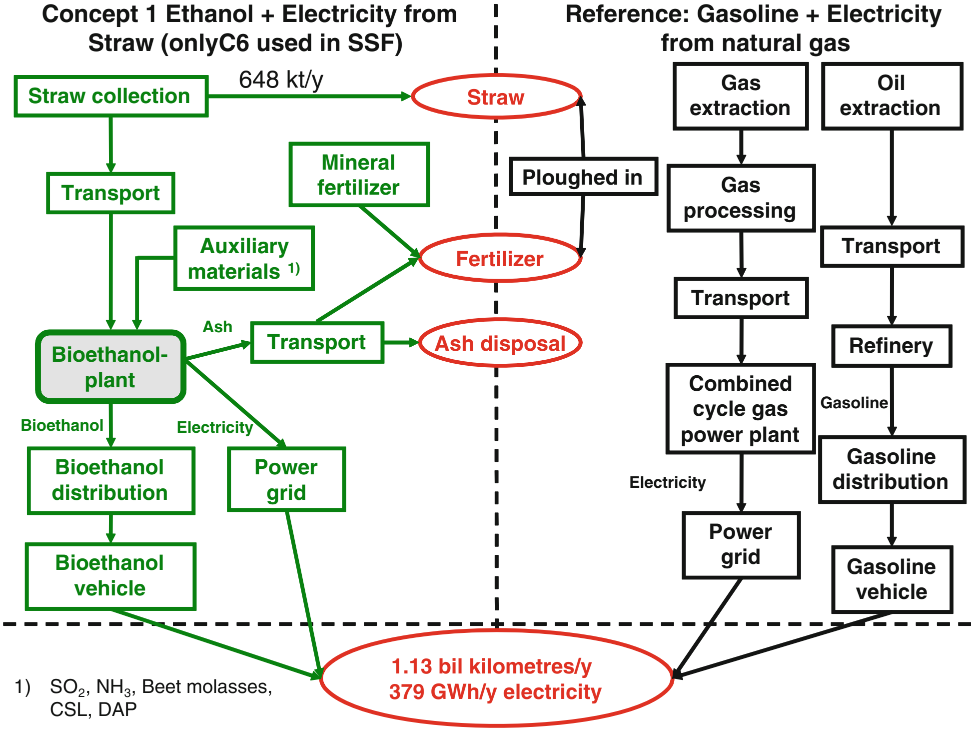


**Fig. 2** LCA based comparison of a bioethanol system (concept 1) with the respective fossil reference system. The boundaries of the bioethanol plant correspond to Fig. 1

In Fig. 3, GHG emissions of two bioethanol systems, one for straw and one for softwood, are shown in kilotons per year (kt/year). In both systems, same amounts of ethanol are produced and all residual materials are burnt to generate electricity. Detailed contributions of each step in the process chain are shown. Total GHG emissions of the softwood system sum up to 114 kt $CO_2$eq/year compared to 160 kt for the straw system. The difference is mainly due to feedstock production and transport and distribution. One should keep in mind, that mineral fertilizer is applied to replace straw taken from the fields whereas no fertilization is necessary in softwood production. Ash returned to the fields in the case of straw cannot replace N fertilizer, which is emission intensive in both, production and application (see Table 2) and accounts for a large share of total emissions in straw production. The higher $CO_2$ emissions in softwood production can be ascribed to the more energy intensive harvest. However, fertilization in the case of straw outweighs these emissions by far.

The second source for higher emissions from the straw system is transportation. The lower density of straw results in longer transport distances which are the reason for higher emissions from transport. Emissions due to transport of ash to field and landfill, which are also included here are small compared to emissions from biomass transport. In both systems, plant auxiliary materials are responsible for a large share of GHG emissions. $CO_2$ originating from combustion of fossil fuels in the energy intensive production processes of auxiliary materials makes up the biggest proportion of these emissions. In principle, reducing the plant capacity would result in a decrease of transport distances and a corresponding decrease of emissions caused by transport. However, according to Slade et al. (2009) the reductions of transport emissions achieved by reducing plant capacity are small and could potentially be outweighed by lower efficiencies or yields in the conversion plant.

As described above, emissions from combustion of residual materials in the ethanol plant do not include $CO_2$ from combustion. However, typical $CH_4$ and $N_2O$ emissions of biomass combustion systems are considered. We assumed identical emissions per MWh of straw and softwood incinerated (see Table 2). The larger emissions from straw in this section are thus due to the lower ethanol yield from straw resulting in higher amount of biomass incinerated in the CHP part of the plant.

Emissions ascribed to the bioethanol vehicle include the emissions that are caused in the production of the vehicle as well as $CH_4$ and $N_2O$ emissions caused by ethanol combustion. Since same amounts of ethanol are used for transport, the emissions of this part of the chain are identical for both systems. Emissions caused by the disposal and construction of the ethanol plant as well as emissions from the sewage treatment are negligible compared to the other contributions.

Figure 4 shows the reductions in GHG emissions compared to the two reference systems. Results for all 13 concepts are summarized. For all concepts, substantial

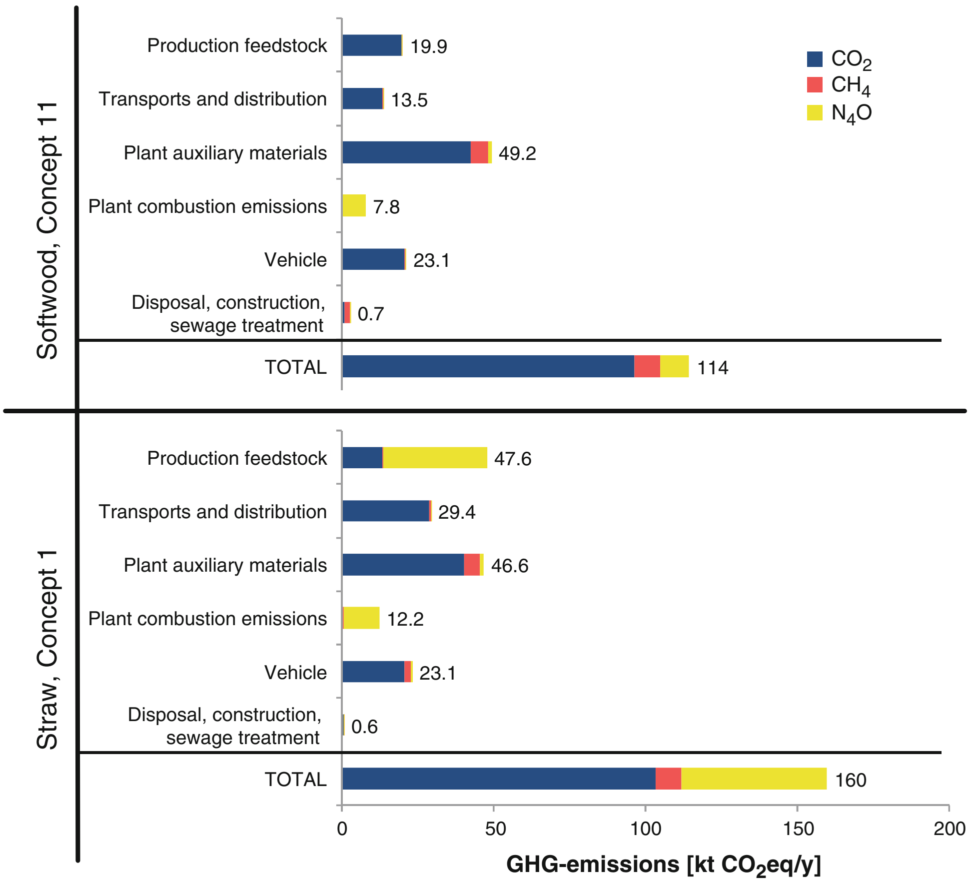


**Fig. 3** Detailed GHG emissions of two bioethanol systems (concepts 1 and 11) producing bioethanol and electricity. Contributions of steps in the process chain are shown

reductions in GHG emissions compared to the fossil as well as the renewable reference system can be achieved. GHG reduction ranges from 41% (vs. renewable reference) to 76% (vs. fossil reference). The highest reductions compared to the fossil reference are attained in concepts 3 and 6. In both scenarios, waste heat from the ethanol production plant is exported as a by-product, whereas in the fossil reference system heat is supplied from a CHP plant, powered by natural gas. Concepts providing district heat were examined for straw only, however, similar behavior would be observed for softwood, since similar amounts of waste heat could supply a district heating grid in the case of softwood too. As expected, in most cases, the reduction of emissions compared to the fossil reference system is much larger than the reduction compared to the renewable reference system. This is especially true for concepts where large quantities of district heat or pellets are produced as a by-product (3–6, 12). When the fossil system is used as a reference large quantities of heat from fossil resources are replaced, whereas renewable heat supplied from biomass is replaced in the case of the renewable reference system. As a consequence, reductions of GHG emissions are significantly lower when the renewable reference system in used. The conversion of C5 sugars in straw to ethanol does not lead to emission reductions when the fossil reference system is used (concept 1 vs. 2 and concept 4 vs. 5). This is due to the fact, that emission reduction caused by higher ethanol yields are canceled by decreased reductions due to lower amounts of by-products. Concepts using C5 molasses as a by-product (concepts 7–9) show the lowest reductions compared to the fossil reference system. This can be explained by the fact, that the production of soy beans, which replace C5 molasses in the reference systems, causes relatively low emissions compared to other by-products.

## Economic evaluation

The economic performance of the concepts was assessed by means of cost comparison analysis. Detailed results for one selected concept as well as specific costs of bioethanol for all concepts are shown.

In Table 6, the results of the cost analysis (costs and revenues) for concept 3 are listed. The annual costs amount to 99.3 M€, of which 29% are capital costs, 12% are fixed operating costs and 59% are variable operating costs. As can be seen, costs of raw material are the dominant expense factor, accounting for 84% of variable operating costs and more than 50% of total costs. This proportion of raw material costs is roughly the same for all concepts.

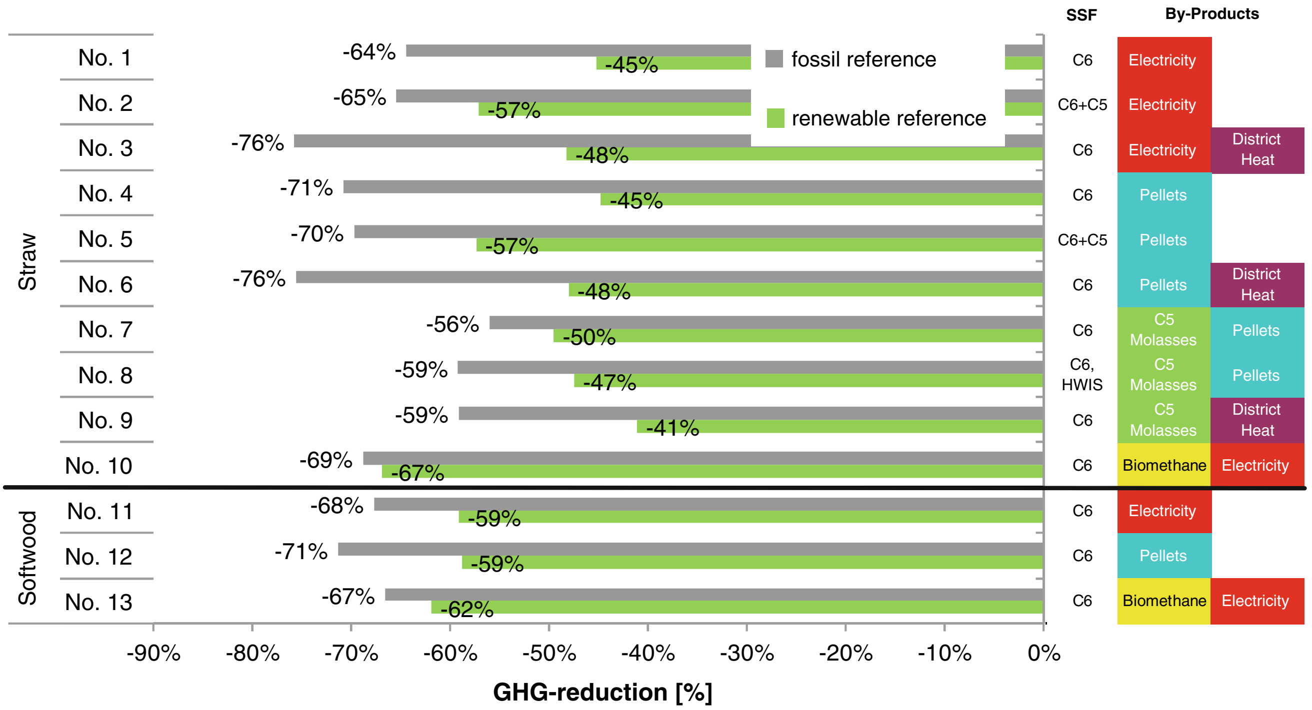


**Fig. 4** GHG reduction of bioethanol systems compared to the fossil and renewable reference systems. Conversion of sugars in SSF and by-products of each concept are shown on the *right side*

**Table 6** Costs and revenues and resulting costs of ethanol for one selected concept (concept 3)

| Costs (M€/year) | |
|---|---|
| Capital costs | −26.3 |
| Fixed operating costs | −11.5 |
| Variable operating costs | |
| Personal | −1.8 |
| Raw material | −51.9 |
| Auxiliary materials | −6.6 |
| Other variable operating costs | −1.2 |
| Sum variable operating costs | −61.5 |
| Total costs | −99.3 |
| Revenues (M€/year) | |
| Electricity | 15.2 |
| Heat | 20.1 |
| Total revenues | 35.3 |
| Total costs bioethanol (M€/year) | 64.0 |
| Spec. costs bioethanol (€/GJ$_{\text{ethanol}}$) | 23.8 |
| Spec. costs bioethanol (€/l$_{\text{gasoline equiv.}}$) | 0.74 |

Annual revenues sum up to 35.3 M€, of which 43 and 57% can be ascribed to the sale of electricity and heat, respectively. The price of electricity was assumed to be 50 €/MWh, corresponding to 50% of the actual feed in tariff for electricity from renewable sources ("Ökostrom"). We assumed conservative 50% of the tariff, because it is uncertain, whether the full tariff will be paid for all of the electricity produced. The price of heat was assumed to be 20 €/MWh, which is a typical value obtained in Austria. The cost of straw was set to 80 €/t (Statistik Austria 2011a). The difference of annual costs and revenues adds up to 64 M€ and is ascribed to the production of 100 kt (ca. 126 ML) of bioethanol. Taking the LHV of ethanol and gasoline into account results in specific costs of bioethanol of 0.74 € per liter of gasoline equivalent.

Sensitivity analysis on bioethanol production cost was carried out for investment and raw material costs as well as for prices of heat and electricity in a range of ±30% of standard values. Results are shown in Fig. 5. As can be seen, variations of raw material and investment costs have a stronger effect on bioethanol costs than variations of prices for by-products. However, none of the factors causes the ethanol costs to leave the price range from 0.5 to 1 €.

In Fig. 6, specific costs of bioethanol for all 13 concepts are shown on energy base. Specific ethanol production costs range from 0.66 to 0.94 €/l$_{\text{gasoline equiv}}$. On principle bioethanol from softwood has lower costs than ethanol produced from comparable concepts using straw (concepts 1 vs. 11, 4 vs. 12 and 10 vs. 13). This effect can be attributed to the lower feedstock costs of softwood as well as to the reduced investment costs which are ultimately a result of the higher content of fermentable sugar. Comparison of concepts with identical by-products but difference in the utilization of sugars in SSF (concept 1 vs. 2, 4 vs. 5) reveals that C5 fermentation could significantly

**Fig. 5** Sensitivity analysis of investment cost, raw material cost, electricity price, and heat price on ethanol cost. Default values (0) were varied by ±30%. Data for concept 3 is shown

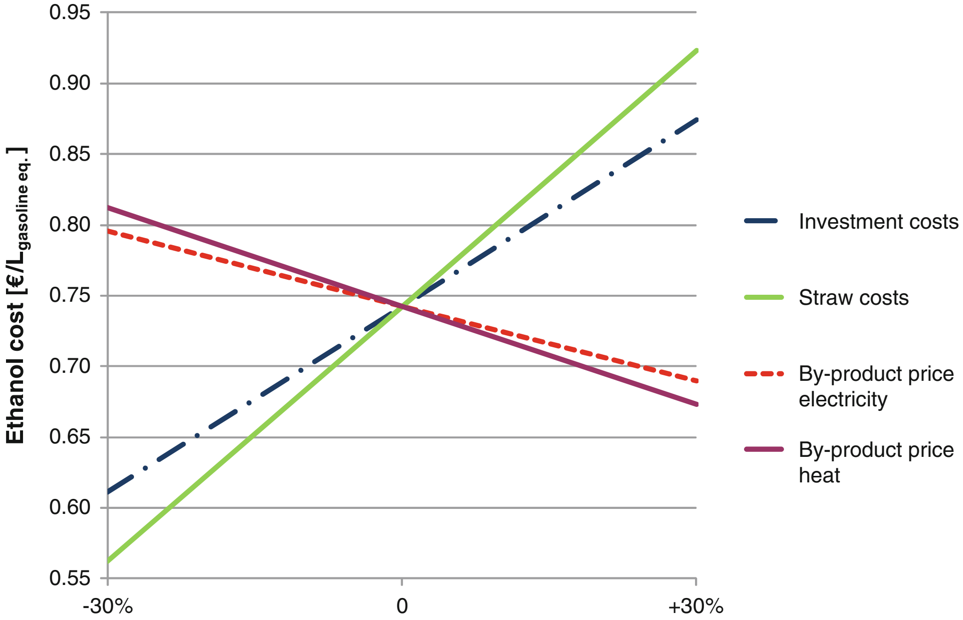
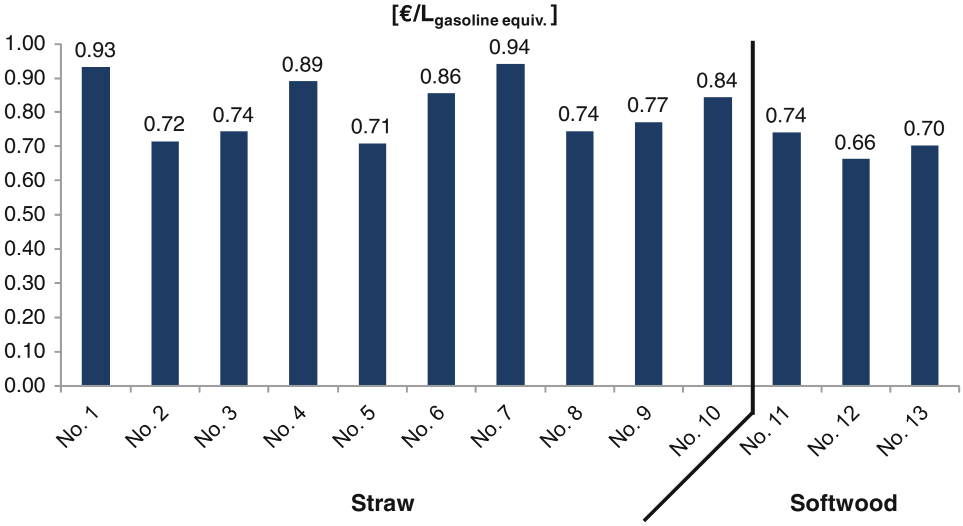


**Fig. 6** Specific costs of bioethanol for 13 production concepts



reduce ethanol costs. This can be ascribed to the fact, that conversion of both types of sugars significantly reduces raw material requirements as well as plant size. As shown in Table 6, associated raw material and investment costs are the largest expense factors.

## Conclusions and discussion

Process simulation of 13 production concepts using steam explosion and SSF showed that process heat and substantial amounts of the potential by-products heat, electricity, pellets, C5 molasses, and biomethane can be obtained from the stillage.

LCA revealed that substantial reductions of GHG emissions with respect to fossil and renewable reference systems can be achieved. This confirms the findings of previous studies (von Blottnitz and Curran 2007; Slade et al. 2009; Balat and Balat 2009, 2010). Reductions relative to the fossil system lie in the range of 56–76%, whereas reductions relative to the renewable reference system range from 41 to 67%. This difference highlights the role renewable by-products play for the GHG mitigation potential of lignocellulosic ethanol. Compared to data published earlier, emission reductions are moderate to comparable. Balat and Balat (2009, 2010) reviewed GHG reductions of lignocellulosic ethanol and found that reductions from 60 to 110% can be achieved, with the majority of data in the 80–100% range. Slade et al. (2009) investigated the same types of biomass and similar processes and found comparable reductions in the base case scenarios (56–82%). In our calculations, biomass production and production of auxiliary materials caused ca. 60% of total emissions of the bioethanol system. The deviation of our results from more optimistic data could therefore potentially be ascribed to these contributions. As far as biomass production is concerned, a possible explanation could be that no fertilizer is taken into account when waste biomass is used as feedstock. When considering auxiliaries, one has to bear in mind that mass flows and type of auxiliaries are largely dependent on the technology applied. Consequently associated emissions can vary greatly, depending on technology. In our calculations land use change effects (Fargione et al. 2008) were not included which can be justified by the fact that the biomass potentials applied do not consider change of land use either.

Economic evaluation of the production concepts yielded bioethanol production costs ranging from 0.66 € to 0.94 € per liter gasoline equivalent. In general, ethanol produced from softwood was found to be slightly cheaper than ethanol from straw. However, if C5 sugars could be converted to ethanol the feedstock specific difference in costs disappears. In all production concepts, the largest cost factors are feedstock costs, amounting to ca. 50–55% of total costs.

Summing up potentials for softwood and straw ca. 340 kt lignocellulosic bioethanol could be produced annually in Austria. However, considering feedstock logistics and potential price rises caused by the increased demand for straw and wood, 100–200 kt per year seem to be a more realistic potential for Austria. Adding 100 kt of lignocellulosic ethanol to the current starch based production capacity of 191 kt, would result in a production capacity corresponding to 10% of the energy consumed as gasoline in Austria in 2009. With the less conservative potential of 340 kt this figure increases to 18%, showing that lignocellulosic ethanol can contribute to renewable transport in Austria, but can never be a sole solution.

However, before commercial production in Austria can take place, some hindrances have to be overcome. The next logical step appears to be the operation of a demonstration scale plant, which could help to further improve process design, troubleshoot technology and clarify questions related to quality, market potentials and still insecure prices of by-products. One key strategy for lignocellulosic ethanol to succeed in Austria could be the integration into existing infrastructure like the pulp and paper industry in the case softwood or conventional ethanol production in the case of straw.

**Acknowledgment** We would like to thank the Austrian Climate and Energy Fund for financing of this study.

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# III. SUMMARY AND CONCLUSIONS

# SUMMARY

The goal of this work was to assess Austrian perspectives for lignocellulosic ethanol production. Based on a detailed review of the technology, thirteen production concepts for the raw materials straw and softwood were developed, simulated and analyzed.

In ***Paper I***, a short review of the technology is presented and an initial set of production concepts (process scenarios) is developed. The raw materials softwood, hardwood, and straw and ethanol production capacities from 50 to 200 kt/year are considered. The conversion technologies size reduction, steam pretreatment, on-site enzyme and yeast production, simultaneous saccharification and fermentation (SSF), distillation and pressure swing adsorption are identical for all of the concepts. Likewise, process heat shall always be supplied by combustion of process residues, aiming at energy self sufficiency. The production concepts differ in i) the type of raw material, ii) the conversion of sugars in SSF, iii) the allocation of process electricity and most importantly iv) in the type of by-products.

During the course of the work the initial set of concepts was refined to obtain the final set of concepts. An analysis of the biomass potentials in Austria showed that the hardwood potential is not sufficient for commercial ethanol production and consequently the hardwood concepts were discarded. Based on the fact that no significant changes in the plant design and the conversion efficiencies are expected for plants with ethanol capacities between 50 and 200 kt/year, the plant capacity was fixed at 100 kt/year. First process simulations showed that large amounts of unused heat are available; as a result the by-product district heat was introduced. Moreover, concepts considering an increased solid content in the fermentation (HWIS) and biogas-production from softwood were included. For the two concepts that deliver biogas as a by-product, upgrading to biomethane was fixed as the only type of biogas utilization. The finalized set consists of thirteen production concepts, three based on softwood and ten based on straw. The by-products electricity, district heat, pellets, C5 molasses and biomethane are considered.

After unit model development the concepts were implemented in IPSEpro. Thereafter process heat integration was performed by means of pinch analysis and heat exchanger network synthesis (see ***Paper II***). The multi stage unit operations distillation and evaporation are in the focus of the pinch analysis because i) these units are energy intensive and therefore have a high potential for heat recovery and ii) their multistage character brings forth many options for heat integration. Moreover, the unit operations steam pretreatment and steam drying play an important role in heat integration. Secondary steam obtained from these units can be used to heat other parts of the process.

Pinch analysis revealed design improvements for the distillation and evaporation sections. These design improvements increase the integration with the background process and thereby reduce the process heat demand. The energy targets that are obtained through pinch analysis are a benchmark for the process heat demand. These targets can be used for an assessment of the efficiency and quality of the heat exchanger network. In combination with energy stream analysis, pinch analysis showed that process residues easily suffice to provide the process with heat. The assumed energy self sufficiency was therefore confirmed. After pinch analysis the design of the process is fixed and a heat exchanger network was synthesized. The optimal heat exchanger network was obtained by minimizing the total cost (energy and investment) of the network. This network was established in IPSEpro. Thereafter the utility or CHP system was implemented and the mass and energy balances were closed. The described procedure guarantees a highly energy efficient production process. As a result a large share of process residues can be used for by-product generation. The significance of by-product generation that was anticipated in the development of concepts was thus confirmed.

In ***Paper III*** and ***Paper V*** the most important simulation results are summarized. For the concepts that consider fermentation of C6 sugars only, some 648 kt of fresh straw (90% dry matter, 583 kt of dry straw) need to be employed to produce the prescribed 100 kt of bioethanol. This corresponds to a process ethanol yield of 78% of the theory, based on C6 sugars. If C5 sugars are also fermented to ethanol, only 446 kt of fresh straw (90% dry matter, 402 kt of dry straw) are necessary. The corresponding process ethanol yields based on all sugars (C5 and C6) and C6 sugars only amount to 70% and 113%, respectively[84]. When softwood is used as a raw material, some 870 kt of fresh biomass (45% dry matter, 391 kt of dry softwood) are necessary for the production of 100 kt ethanol. Because of the higher moisture content of softwood, significantly higher amounts of fresh biomass need to be provided; however, on a dry basis less biomass is necessary. Interestingly, the process ethanol yield based on C6 sugars amounts to 78%, the same value that is obtained for straw[85]. In all concepts significant amounts of by-products are obtained. For detailed mass balances see Appendix C.

In Fig. S 1 the energy efficiencies of the production concepts are summarized. As can be seen, between 24% and 43% of energy in the biomass can be recovered in the ethanol product. In general, the concepts that use wood as a raw material have higher energy efficiencies. This is for two reasons: on the one hand wood contains a higher amount of

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[84] *The lower process yield based on C5 and C6 sugars is a result lower conversion of C5 sugars during pretreatment and fermentation.*

[85] *Based on the literature review (section 2), different values for the conversions in the single unit operations were applied for the different types of feedstock. However, in the overall process the differences cancel each other out and lead to the same process ethanol yield.*

convertible sugars, and on the other hand the higher moisture content of fresh wood (55% vs. 10% for straw), results in a lower LHV of wood. As described above (section 3.1.3) in all concepts, process heat is provided by burning part of the stillage. Nonetheless, significant amounts of residual biomass are available for by-product generation. These by-products have a significant impact on the energy efficiencies of the concepts, as can be seen in Fig. S 1. As a result, process energy efficiencies up to 78% can be achieved. Highest efficiencies are reached for concepts that provide district heat (concepts 3, 6, 8 and 9) or the relatively unrefined by-products C5 molasses (7-9) and pellets (4-6, 12), whereas lowest efficiencies are obtained for concepts with electricity generation (1, 2 and 11). The lower energy efficiencies of concepts with electricity production can be ascribed to the energy losses during electricity generation. However, for a complete assessment of the different types of by-products the different prices and markets have to be considered. In these aspects the well established by-product electricity definitely outperforms district heat, pellets and C5 molasses.

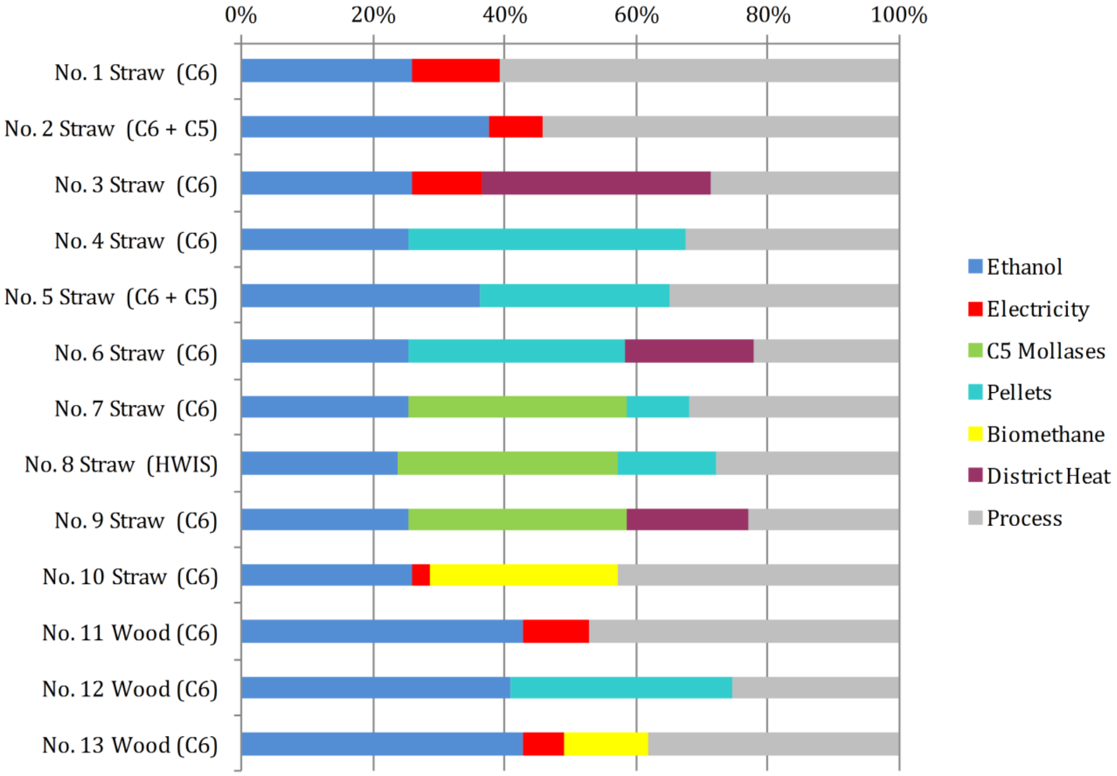

*Fig. S 1: Energy efficiencies of the production concepts according to equation (18) (see section 3.4.1)*

The combined production of bioethanol, biomethane and electricity, as discussed in ***Paper IV,*** is of particular interest. On the one hand well established by-products are obtained and on the other hand higher efficiencies are obtained than in concepts that provide electricity[86]. However, most research efforts are still necessary for these concepts, because little experimental data is available for the anaerobic digestion (AD) of lignocellulosic stillages. Many decisive performance parameters such as the methane yield and the residence time have yet to be confirmed in large scale. Lower methane yields or higher residence times would lead to less biogas or significantly higher reactor volumes which could challenge the feasibility of these concepts. When $SO_2$ or $H_2SO_4$ are used for the pretreatment, sulfur inhibition might occur during AD of lignocellulosic stillages, in particular when softwood stillage is converted to biogas. In conventional, smaller scale biogas production the digestate is usually recycled to the fields to complement or replace mineral fertilizer. This strategy is crucial for the environmental friendliness of existing biogas plants. For the large scale production of biogas from lignocellulosic stillage this strategy may not be feasible and consequently this benefit of AD technology can not be exploited. The disposal of anaerobic and aerobic sludge that is formed in these concepts may be a challenge.

In ***Paper V*** the results of the greenhouse gas (GHG) life cycle analysis (LCA) and the economic assessment are presented. In LCA the system boundary of the analysis is expanded beyond the bioethanol plant to also include all emissions from cultivation of the biomass to deployment of end energy (well to wheel). The thus obtained bioethanol systems are compared to two reference systems that produce the same amount of ethanol and by-products. For the bioethanol production systems, feedstock production and production of plant auxiliary materials are the steps that cause the largest share of GHG emissions. However, compared to both reference systems the GHG emissions of the bioethanol systems are small and consequently substantial emission reductions can be achieved. When the GHG emissions of the fossil systems are used as a reference, the GHG emissions can be reduced by 56% to 76%. The renewable reference systems cause less GHG emissions than the fossil reference systems. As a result, the bioethanol system reduces GHG emissions compared to the renewable reference system by only 41% to 67%. The difference between renewable reference and fossil reference can be ascribed to the renewable by-products. This difference illustrates the fact that by-products are important not only for the energy efficiency but also for the ecologic performance of lignocellulosic ethanol production. On average, the concepts that use softwood as a feedstock perform slightly better than those with straw. This is mainly based on the lower emission during i) feedstock cultivation and harvest and ii) transport and distribution. Upon comparison of the different by-products one can see how the by-products influence GHG mitigation of the production concepts. In this respect the concepts with district heat perform very well, particularly against the fossil reference, in which large amounts of heat are provided by fossil energy carriers. This causes a great amount of $CO_2$ emissions that are avoided in the

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[86] *Methane and electricity are certainly by-products that are best established.*

respective bioethanol systems. The concepts that provide C5 molasses show the poorest performance, which can be explained by the fact, that the production of soy beans that replace C5 molasses in the reference systems, causes relatively low emissions compared to other by-products.

To assess the economic performance of lignocellulosic ethanol production cost comparison analysis was applied. Using this method, annual costs are compared to annual revenues (from by-products). Ethanol costs are calculated as the difference that is necessary to break even. Accounting for some 50% of total costs, raw material costs are the biggest expense factor. The second larges expense factor is investement cost, which accounts for up to 27% of total costs. Revenues obtained from by-products have a significant impact on the economic performance. For all concepts, ethanol production costs are below 1 € per L gasoline equivalent (0.66 to 0.94). There is not one concept that clearly outperforms the others from an economic point of view but direct comparison of similar concepts (i.e. concepts that are identical in all aspects but one) leads to some interesting insights and clearly shows which strategies should be followed for cost effective lignocellulosic ethanol production:

- For concepts with straw as a feedstock, there is a clear economic advantage for concepts with **C5 fermentation** (concept 1 vs. 2, 4 vs. 5). This is due to the lower demand of feedstock and due to the lower investment cost (smaller plant size).
- There is a clear economic effect of a **high solid content (HWIS)** during fermentation (7 vs. 8). The concept with higher solid content during fermentation has significantly lower cost, which can be ascribed to the significantly lower investment costs.
- There is a clear economic effect of the **feedstock** (e.g. 1 vs. 11): The concepts with softwood as feedstock perform better than the concepts with straw. This can be ascribed to the higher ethanol yield per kg of dry biomass and the lower feedstock costs that were assumed.
- An interesting observation can be made for the concepts that provide **district heat.** District heat as a by-product is economically feasible only when it is produced in combination with electricity i.e. in a combined heat and power (CHP) plant (1 vs. 3). This is due to the fact, that energy (heat) that would otherwise be wasted is commercialized in the CHP concept (1). This is also reflected in the significantly higher energy efficiency of the concept. On the other, district heat as a by-product to pellet production, does not significantly impact the economic performance (4 vs. 6). Here, heat merely substitutes pellets; likewise the energy efficiency of the district heat concept is only slightly higher than that of the pellet concept.

As described above, some by-products perform better than others in the analysis; however, before delivering a judgment about which by-product is the most promising, one should also take a look at the difference in technical maturity, flexibility and market potentials of the different by-products. These factors will crucially influence the success of a technology.

- The combustion of process residues is probably the biggest technical challenge for the generation of the by-product **electricity**. However, since electricity generation is also considered in a planned commercial plant in Italy (Chemtex in Crescentino), it can be regarded as technically mature. Moreover, the combustion of process residues is also encountered during the generation of process heat, which is part of all concepts. The market maturity, flexibility and market size can be taken for granted.
- The manufacture of the by-product **pellets** is technically relatively simple. However, market maturity and market size are at present uncertain. If the pellets can be produced at a quality that allows for combustion in domestic stoves, this by-product is definitely an attractive solution. Due to the lower ash content and the respective ash composition softwood pellets are more suitable for application in domestic stoves than straw pellets. However, for both types of pellets a washing step for the removal of undesired compounds may be necessary.
- **District heat** as a by-product is technically mature and can significantly increase the efficiency of the plants, and also in ecologic and economic aspects the district heat concepts perform well. However, there are two major disadvantages of the by-product district heat: First, at an ethanol plant capacity of 100 kt bioethanol, very large amounts of district heat are generated. It is questionable, whether in Austria there exists a location at which this amount of heat is demanded. Second, the demand for district heat is seasonally limited. A strategy that could help overcome these two disadvantages is to provide heat for other industries rather than district heat. However, these industries must require large amounts of heat at the temperature levels available.
- **C5 Molasses** are obtained through evaporation of the liquid fraction of straw stillage. The manufacture of this by-product has been proven in demo scale [Larsen *et al.* , 2012]. As far as the utilization of C5 molasses is considered, two options exist: the valorization as animal feed[87] and the co-digestion in conventional biogas plants as so-called biogas booster. For both options the market maturity and size are questionable.
- The project results showed that **Biomethane** (obtained through anaerobic digestion of the stillage and subsequent up-grading) is a promising by-product.

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[87] *Which was assumed in LCA calculations.*

Market size, maturity and flexibility can be taken for granted. However, the technical performance and maturity of anaerobic digestion of lignocellulosic stillage are still uncertain. In this field, there is definitely demand for R&D.

# CONCLUSIONS & OUTLOOK

Compared to conventional feedstock lignocellulosic biomass contains and relatively large share of non-fermentable components. Therefore, after fermentation and separation of ethanol, a large share of the energy that is fed to the process as biomass is recovered in the process residues (stillage). These process residues contain enough energy to provide the process with heat. Energy self sufficiency of the process can thus be achieved. In addition to that substantial amounts of by-products can be recovered from the stillage. These by-products have a significant positive influence on the energetic (energy efficiency), the ecologic (GHG mitigation) and the economic (ethanol cost) performance of ethanol production from both softwood and straw. Since process heat and by-products are both obtained from process residues, the amount of by-products is inversely proportional to the heat demand of the process. Energy efficiency achieved through process heat integration reduces the process heat demand and is therefore crucial to maximize the amount of by-products and thus improve the performance and the sustainability of the technology.

The production concepts that were developed, simulated and analyzed within this work are all characterized by efficient use of process heat. Consequently, they perform quite well as far as the above described parameters are concerned. Particularly the energy efficiency and the GHG mitigation potential of the technology are promising which can partly be ascribed to the positive effect of the by-products.

As far as the different by-products are concerned, there is no clear answer, which by-product is most promising. **Electricity** is very well established but performs only moderately well, which is due to the relatively low efficiencies. However, in combination with district heat generation, C5 fermentation (straw) or with softwood as a feedstock, the electricity concepts show good results. The concepts with the **district heat** perform very well, however, the demand of district heat is temporally and locally limited. **C5 molasses** are probably the least attractive by-product which is due to their relatively poor performance and the uncertain market potential. **Pellets** perform quite well, in particular with C5 fermenation (straw) or softwood as a feedstock; when pellets have the quality for incineration in domestic stoves, there will certainly a demand for this by-product. Just as electricity, **Biomethane** is very well established. In addition the performance is better, however, the technology is less developed and more research is still required.

A comparison of the different types of lignocellulosic biomass shows that softwood is the more attractive choice. On average, the concepts with softwood yield higher energy efficiencies, lower ethanol prices and cause less GHG emissions.

Based on the material balances and Austrian biomass potentials, some 250 kt/y or 6.7 PJ of lignocellulosic ethanol are calculated as a realistic medium term potential for Austria (ca. 100 kt from spruce and 150 kt from straw). This value corresponds to 55% of the theoretical potential calculated in section 2.1. Adding these potential 250 kt of lignocellulosic ethanol to the 191 kt or 5.3 PJ of grain based ethanol that can presently be produced in Austria, a total ethanol potential of 12 PJ is obtained. This amount corresponds to 15% of the gasoline fuels (based on energy), that were sold in Austria in 2010. A full exploitation of the lignocellulosic biomass potential could therefore be a strategy to meet the 2020 goals of 10% of renewable energy in transport. This goal could be reached without import of additional biomass or allocation of additional land. Substantial greenhouse gas saving would be attained and large amount of renewable by-products would be generated. In this vision, one or two facilities run on woody biomass and two facilities run on straw would need to be erected.

However, there are still many hindrances that have to be overcome to reach this goal or at least go a first step in this direction.

First, with 0.7 – 0.9 €/L gasoline equivanlent the prices are still too high to be competitive. Ethanol from sugarcane is produced at prices around 0.3 €/L [Dias *et al.* , 2010] and ethanol from starchy crops at prices ranging from 0.3 to 0.7 €/L [Kwiatkowski *et al.* , 2006, Gwehenberger *et al.* , 2007]. To decrease the ethanol prices further technology development and technological learning is necessary. In this context, the following research fields can be identified:

- **Process technologies:** the process steps pretreatment, enzymatic hydrolysis and fermentation are crucial for efficient ethanol production. Clearly, a lot of research efforts have already been dedicated to these fields. Nonetheless, improvements in these fields and particularly the integration of the process steps (e.g. consolidated bioprocessing) can still lead to significant improvements of the technology. Moreover, separation technologies will play an important role in future biorefineries.
- **Fermentation of C5 sugars**: The results of this work showed that for the straw concepts C5 fermentation strongly enhances the performance.
- **Enzyme technology:** In the concepts considered, on-site enzyme production was assumed. Further advancements in this field will for sure influence the technology positively.

- **By-products:** Some promising by-products considered in this still work still require additional research to reach technical maturity:
    - **Biomethane:** the large scale anaerobic digestion of lignocellulosic stillage is a field that requires research.
    - **Pellets:** the quality and application of pellets in domestic stoves should be investigated.

  In addition to the by-products that were investigated within this work, research should be directed at the recovery of additional and advanced by-products. Possible strategies for new by-products are:
    - **$CO_2$ separtion from fermentation**: the $CO_2$ that is obtained from fermentation, yeast propagation and enzyme production is almost pure and could be recovered without major technical effort. A large range of applications is possible.
    - **Gasification of process residues:** the provision of synthesis gas would open a whole new branch of by-products.
    - **By-products from C5 sugars:** If C5 sugars are not fermented to ethanol, a strategy for the valorization of this stream could push the technology forward, in particular for straw.
- **Integration with other industries:** the integration with other industries could result in major performance improvements. Large amounts of heat are generated in the ethanol production process. If that heat can be used in other production processes the overall efficiency of the combined production site can be increased. This affects both the production economics and the environmental impact positively. Moreover, a common infrastructure (feedstock logistics, utilities, waste disposal, water treatment,…) will reduce the investment and improve the production costs. Possible industries for integration are the pulp and paper industry for softwood or conventional ethanol production for straw. In the latter case, even higher degrees of integration are possible (e.g. common rectification).

In addition to these strategies that improve the technology and reduce the ethanol cost, another key question that must be addressed is feedstock supply. Huge amounts of feedstock are necessary and with 50% of total cost, feedstock cost is the major driver of ethanol cost. The calculations that were made within this work only give a first insight about the biomass potential in Austria but do certainly not suffice to guarantee affordable and sustainable supply of straw and woody biomass. Detailed economic modeling of biomass availability is therefore necessary and will also help finding potential locations for a plant.

Finally policy and financing issues will have to be addressed if lignocellulosic ethanol shall become a commercial reality in Austria. Due to the complicated technology that is necessary to access the sugars in lignocellulosic biomass and obtain ethanol and the by-products, ethanol from lignocellulosic biomass strongly depends on the economies of scale principle. Therefore it will stay a centralized technology that requires tremendous investment costs and long payback periods. A stable political, economic and legal framework is crucial to attract potential investors.

If all these criteria are met, lignocellulosic ethanol will hopefully soon unlock its potential and contribute to sustainable energy supply in Austria.

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# IV. APPENDICES

# APPENDIX A: DEVELOPMENT OF THE APP_BIOLIB_LIGNO

The library **APP_BioLib_Ligno** was developed within this work based on the **APP_BioLib**. The modeling concept applied is therefore identical to the one of the **APP_BioLib,** [Schausberger *et al.* , 2010]. Therefore, in this Appendix only the modifications compared to the APP_BioLib are explained. For all the models described in this section, a unit model flowsheet is available in electronic form.

## GLOBAL MODELS

### *BIOFUEL GLOBAL – NEW GLOBAL*

#### DESCRIPTION

This model was developed to balance the liquid organic compounds that occur in the process. In the APP_BioLib ethanol is the only liquid besides water that is considered; the biofuel global is introduced, but cannot be used.

Now, in the APP_BioLib_Ligno, in addition to ethanol glycerol, acetic acid and furfural can be balanced. For simplicity reaosns, furfural is used to balance both furfural and hydroxymethylfurfural. The formation of these liquid compounds according to equations xyz is considered in the respective unit operations. In the global, only the mass fraction of these units is considered.

#### VARIABLES

| | | |
|---|---|---|
| etoh | Mass fraction ethanol | [kg/kg] |
| glycerol | Mass fraction glycerol | [kg/kg] |
| acetic_acid | Mass fraction acetic acid | [kg/kg] |
| furfural | Mass fraction furfural and hmf | [kg/kg] |

#### EQUATIONS

##### Mass Fractions

The sum of mass fractions of the components is equal to 1. Unit: kg/kg

```
f1:          1.0 = etoh + glycerol + acetic_acid + furfural;
```

##### Test section

The mass fraction of the single species must be ≥0 and ≤ 1.

```
tminetoh:    test(etoh <= 1.0)           warning "etoh > 1.0";
tmaxetoh:    test(etoh >-1e-6)           warning "etoh < 0.0";
tminglyc:    test(glycerol <= 1.0)       warning "glycerol> 1.0";
tmaxglyc:    test(glycerol>-1e-6)        warning "glycerol < 0.0";
tminhac:     test(acetic_acid<= 1.0)     warning "acetic_acid > 1.0";
tmaxhac:     test(acetic_acid>-1e-6)     warning "acetic_acid < 0.0";
tmin:        test(furfural <= 1.0)       warning "furfural > 1.0";
tmax:        test(furfural >-1e-6)       warning "furfural < 0.0";
```

### *WEENDER GLOBAL – MODIFICATIONS*

#### DESCRIPTION

The weender global is used to specify the biomass components according to a modified weender analysis [Schausberger *et al.* , 2010]. It was developed in the APP_BioLib, however, to repersent all the species that prevail in the processes considered, some species were added in the APP_BioLib_Ligno. In particular, the different types of monomeric sugars (C5 and C6) can now be distinguished. Instead of the variable CH_sugar, that was used to represent all monomeric sugars in the APP_BioLib, monomeric C5 and C6 sugars are represented by means of the variables CH_mono_C5 and CH_mono_C6. Following the same principle, the variable P_bact that was used in the APP_BioLib to represent all microbial protein, is now split into the two variables P_bact_ext and P_bact_int. These variables rerpesent the mass fraction of extracellular Protein (e.g. Cellulase enzyme) and intrcallular Protein (i.e. all other protein). Below, the new variables are shown in bold characters.

## VARIABLES

| | | |
|---|---|---|
| CH_bact | Mass fraction of microbial carbohydrates | [kg/kg] |
| CH_starch | Mass fraction starch | [kg/kg] |
| **CH_mono_C5** | **Mass fraction of monmeric C5 sugars** | **[kg/kg]** |
| **CH_mono_C6** | **Mass fraction of monmeric C6 sugars** | **[kg/kg]** |
| CH_cell | Mass fraction of cellulose | [kg/kg] |
| CH_hemicell | Mass fraction of hemicellulose | [kg/kg] |
| CH_lignin | Mass fraction of lignin | [kg/kg] |
| **P_bact_int** | **Mass fraction microbial proteins, intrazellular** | **[kg/kg]** |
| **P_bact_ext** | **Mass fraction of extracellular protein, e.g. cellulase enzyme** | **[kg/kg]** |
| P_plant | Mass fraction proteins plant | [kg/kg] |
| L_bact | Mass fraction micorbial lipids | [kg/kg] |
| L_fats | Mass fraction plant lipids | [kg/kg] |
| ash | Mass fraction of ash/inorganics | [kg/kg] |
| v | Specific volume of biomass | [$m^3$/kg] |
| Dispersed (No, Yes) | A switch which is used to decide wether Biomass is dispersed in liquid. If yes v (specific volume) is set according to [Wooley & Putsche, 1996] (rho = 1.5 $g/cm^3$). Otherwise (wood logs, straw bales etc..), v has to be specified (switch). | |

## EQUATIONS

### Mass Fractions & specific volume

The sum of mass fractions of the components is equal to 1. Unit: kg/kg

```
f1:           1.0 = CH_bact + CH_starch + CH_mono_C5 + CH_mono_C6 + CH_cell + CH_hemicell + CH_lignin
+ P_bact_int + P_bact_ext + P_plant + L_bact + L_fats + ash;
```

If the switch “Dispersed” is set to yes, the specific volume v, is set to a fixed value. Otherwhisem v has to be specified. Unit: $m^3$/kg.

```
ifl           Dispersed == Yes then
v1:           v=0.0006667;
endifl
```

### Test section:

The mass fraction of the single species must be ≥0 and ≤ 1.

```
tminCHbact:   test(CH_bact <= 1.0)          warning "CH_bact > 1.0";
tmaxCHbact:   test(CH_bact >= -1e-6)        warning "CH_bact < 0.0";
tminstarch:   test(CH_starch <= 1.0)        warning "CH_starch > 1.0";
tmaxstarch:   test(CH_starch >= -1e-6)      warning "CH_starch < 0.0";
tminC5:       test(CH_mono_C5<= 1.0)        warning "CH_mono_C5> 1.0";
tmaxC5:       test(CH_mono_C5 >= -1e-6)     warning "CH_mono_C5< 0.0";
tminC6:       test(CH_mono_C6<= 1.0)        warning "CH_mono_C6> 1.0";
tmaxC6:       test(CH_mono_C6 >= -1e-6)     warning "CH_mono_C6< 0.0";
tmincell:     test(CH_cell <= 1.0)          warning "CH_cell > 1.0";
tmaxcell:     test(CH_cell >= -1e-6)        warning "CH_cell < 0.0";
tminhcell:    test(CH_hemicell <= 1.0)      warning "CH_hemicell > 1.0";
tmaxhcell:    test(CH_hemicell >= -1e-6)    warning "CH_hemicell < 0.0";
tminlignin:   test(CH_lignin <= 1.0)        warning "CH_lignin > 1.0";
tmaxlignin:   test(CH_lignin >= -1e-6)      warning "CH_lignin < 0.0";
tminPbacte:   test(P_bact_ext <= 1.0)       warning "P_bact_ext > 1.0";
tmaxPbacte:   test(P_bact_ext >= -1e-6)     warning "P_bact_ext < 0.0";
tminPbacti:   test(P_bact_int <= 1.0)       warning "P_bact_int> 1.0";
tmaxPbacti:   test(P_bact_int  >= -1e-6)    warning "P_bact_int < 0.0";
tminPplant:   test(P_plant <= 1.0)          warning "P_plant > 1.0";
tmaxPplant:   test(P_plant  >= -1e-6)       warning "P_plant < 0.0";
tminLbact:    test(L_bact <= 1.0)           warning "L_bact > 1.0";
tmaxLbact:    test(L_bact  >= -1e-6)        warning "L_bact < 0.0";
tminLfats:    test(L_fats <= 1.0)           warning "L_fats > 1.0";
tmaxLfats:    test(L_fats  >= -1e-6)        warning "L_fats < 0.0";
tminash:      test(ash <= 1.0)              warning "ash > 1.0";
tmaxash:      test(ash  >= -1e-6)           warning "ash < 0.0";
```

# CONNECTION MODELS

## *BIOSTREAM CONNECTION – MODIFICATIONS*

### DESCRIPTION

In IPSEpro, connection models are used to transfer data from one unit to another [Perz & Bergmann, 2003]. In a phyiscal sense, connection models are typically used to represent stream data. The biostream is used to handle data of streams that contain a mixture of i) water, ii) solid biomass compounds , iii) liquid compounds and iv) dissolved CO2.

Water is represented by the variable w_water. Solid biomass compounds are represented by the variable w_drymatter and are specified either by a Weender global or an Elementary global. If a Weender gobal is used, insolubles and solubles are distinguished and the content of water insoluble solids (WIS) is calculated. Liquid compounds other than water are represented by the variable w_biofuel. If a Biofuel global is referenced, the single species (ethanol, furfural, acetic acid and glycerol, see above) are balanced If no Biofuel global is referenced, w_biofuel represents ethanol only. If an Elementary global is used to represent organic compounds, it is used to represented all organic matter, i.e. solids and liquids! Therefore, it can only be used alone, i.e. without referencing a Biofuel or a Weender global at the same time.

### GLOBALS

biofuel: Biofuel (optional)
weender: Weender (optional)
elementary: Elementary (optional)

### VARIABLES

| | | |
|---|---|---|
| p | Pressure | [bar] |
| t | Temperature | [°C] |
| h | Specific enthalpy of the stream | [kJ/kg] |
| v | Specific volume of the stream (i.e. of a mixture of biomass and water) | [m³/kg] |
| mass | Mass flow | [kg/s] |
| w_water | Mass fraction of water in the stream | [kg/kg] |
| w_biofuel | Mass fraction of biofuel | [kg/kg] |
| w_drymatter | Mass fraction dry matter | [kg/kg] |
| w_composition | Mass fraction of CO2. | [kg/kg] |
| wis | Mass fraction of water insoluble solids (WIS) | [kg/kg] |

### EQUATIONS

#### **General section**

#### Mass Fractions

The sum of mass fractions of the components is equal to 1. Unit: kg/kg

```
m1:            1.0 = w_water + w_biofuel + w_drymatter + w_composition;
```

Depending on the setup of Globals, six different cases can be distinguished. In cases 1a – 1c, the Biofuel global is referenced, whereas in cases 2a – 2c the Biofuel global is not referenced. In cases a, neither Weender nor Elementary globals are refernced. These cases apply, when the stream does not contain any drymatter (w_drymatter =0). In cases b, the drymatter is specified by a Weender global, whereas in cases c, it is specified by an Elementary global. For all the cases, the biostream variables are cacluated in this section. For simplicity reasons, equations for the case 1b are shown only (it is the most frequently used case). The other cases (1a, 1c, 2a, 2b, 2c) can be explored by opening the library in IPSEpros model development kit (MDK).

#### **Case specific section**

#### Specific section for case 1a is not included

```
ifl            ref(Biofuel) && !ref(Elementary) && !ref(Weender) then
…
endifl
```

#### Specific section for case 1b

```
ifl            ref(Biofuel) && !ref(Elementary) && ref(Weender) then
```

The enthalpy of the stream is calculated as linear combination of the temperature dependent enthaplies of the stream components (water, biomass, biofuel and composition). Unit: kJ/kg

```
    ft1b:           h = fhpt(p, t, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) * w_water + fh_etohl(p, t) * w_biofuel + (fhpt(p, t, 0,
    0, 0, 0, 0, 0, 1.0, 0, 0, 0, 0, 0, 0) + 348.24) * w_composition + fht_biomass (t)* w_drymatter;
```

The specific volume of the stream is calculated. Unit: $m^3$/kg

```
    fv1b:           if (w_composition==1) then
                    v = fv(p, fhpt(p, t, 0, 0, 0, 0, 0, 0, 1.0, 0, 0, 0, 0, 0, 0), 0, 0, 0, 0, 0, 0, 1.0, 0, 0, 0, 0, 0, 0) *
                    w_composition;
    else
                    v = (fv(p, fhpt(p, t, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0), 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) * w_water
    + fv_etohl(p, t) * w_biofuel + Weender.v * w_drymatter)/(w_drymatter+w_water+w_biofuel);
```

The content of water insoluble solids is calculated. In this context it is assumed that cellulose, hemicellulose, lignin, starch, yeast and 50% of the ash are insoluble, whereas the other Weender species are soluble. Unit: kg/kg

```
    wis1b:          wis = w_drymatter * (Weender.CH_hemicell + Weender.CH_cell +  Weender.CH_lignin +
    Weender.CH_starch + Weender.CH_bact + Weender.P_bact_int + Weender.L_bact + 0.5 * Weender.ash )
    endifl
```

## Specific section for cases 1c, 2a, 2b and 2c are not included

```
    ifl             ref(Elementary) && ref(Biofuel) && !ref(Weender) then
    …
    endifl
    ifl             !ref(Biofuel)  && !ref(Elementary) && !ref(Weender) then
    …
    endifl
    ifl             !ref(Biofuel) && !ref(Elementary) && ref(Weender) then
    …
    endifl
    ifl             !ref(Biofuel) && ref(Elementary) && !ref(Weender) then
    …
    endifl
```

## Test section

In the test section, it is checked whether the mass flow and all mass fractions are positive.

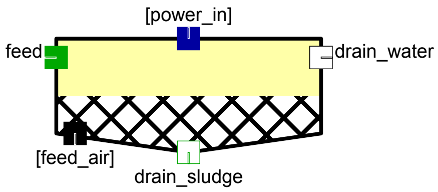
```
    t1:             test (mass >= 0.0) warning "mass flow negative";
    t2:             test (w_water >= -1e-5) warning "w_water negative";
    t3:              test (w_biofuel >= -1e-5) warning "w_biofuel negative";
    t4:             test (w_drymatter >= -1e-5) warning "w_drymatter negative";
    t5:              test (w_composition >= -1e-5) warning "w_composition negative";
```

When neither Elementary nor a Weender global are referenced, the the drymatter must be zero.

```
    ifl     !ref(Elementary) && !ref(Weender) then
    tg2:            test(w_drymatter < 1e-6)        warning"Define dry matter by a elementary or weender global object
    or set w_drymatter to 0";
endifl
```

# UNIT MODELS

## *BF_AEROBIC_STAGE – NEW UNIT*



### DESCRIPTION

A simplified model for aerobic water treatment. Carbon, Oxygen and Hydrogen in the feed are converted to $H_2O$ and $CO_2$ according to aerobic metabolism ( see equation (11)). All other elements of organic matter in the feed are recovered in the sludge. This model can be used to calculate basin sizes, power demand and air demand, that are necessary for aerobic water treatment. The removal of COD has to be calculated with external monitor units. Elementary globals must be used to specify organic copmounds.

### CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain_sludge |
| stream: | drain_water |
| stream: | feed_air (optional) |
| shaft: | power_in (optional) |

### VARIABLES

| | | |
|---|---|---|
| t | Temperature in the basin | [°C] |
| dt_feed | Temperature difference between feed and temperature in reactor | [°C] |
| p | Pressure in the basin | [bar] |
| dp_feed | Pressure drop of the feed | [bar] |
| dp_air | Pressure drop of air | [bar] |
| conversion | Conversion of organic matter to CO2 and H2O | [%] |
| excess_O2 | Excess amount of O2 vs. stoichiometric demand | [%] |
| O2_demand | Stoichiometric oxygen demand | [kg/s] |
| CO2_formed | Amount of CO2 that is formed due to aerobic conversion | [kg/s] |
| sludge_moisture | Moisture content of the sludge | [kg/kg] |
| HRT | Hydraulic retention time | [d] |
| volume | Volume of the basin | [m³] |
| depth | Depth of the basin | [m] |
| spec_power_in | Specific power input of stirrers | [kW/m³] |

### EQUATIONS

#### General mass balance

The overall mass of drymatter, water, oxygen and carbon dioxide are maintained. Units: kg/s

omb1: feed.mass + O2_demand = drain_sludge.mass + drain_water.mass + CO2_formed;

#### Mass balance for stream components

The water balance has to be omitted. Drymatter is converted to a certain extent. Units: kg/s

mbdm1: feed.mass * feed.w_drymatter * (1-conversion) = drain_sludge.mass * drain_sludge.w_drymatter;

Formally biofuel is recovered in the sludge. In practice, all organic matter is part of the elementary global. Units: kg/s

mbbf: feed.mass * feed.w_biofuel = drain_sludge.mass * drain_sludge.w_biofuel;

Formally $CO_2$ from the feed is recovered in the sludge. In practice, no CO2 will be present in the feed. Units: kg/s

mbco: feed.mass * feed.w_composition = drain_sludge.mass * drain_sludge.w_composition;

#### Elementary balance and composition of drain

The conversion of drymatter conversion is modeled with one conversion, i.e. the conversion of C, H, and O are identical. All other elements of drymatter in the feed are recovered in the sludge. The ash balance is omitted. Unit: kg/s

mbeC: drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myC = feed.mass * feed.w_drymatter * feed.Elementary.myC * (1 - conversion);

```
    mbeH:         drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myH = feed.mass *
    feed.w_drymatter * feed.Elementary.myH * (1 - conversion);
    mbeN:         drain_sludge.mass  * drain_sludge.w_drymatter * drain_sludge.Elementary.myN = feed.mass *
    feed.w_drymatter * feed.Elementary.myN;
    mbeO:         drain_sludge.mass  * drain_sludge.w_drymatter * drain_sludge.Elementary.myO = feed.mass *
    feed.w_drymatter * feed.Elementary.myO * (1 - conversion);
    mbeS:         drain_sludge.mass  * drain_sludge.w_drymatter * drain_sludge.Elementary.myS = feed.mass *
    feed.w_drymatter * feed.Elementary.myS;
    mbeCl:        drain_sludge.mass  * drain_sludge.w_drymatter * drain_sludge.Elementary.myCl = feed.mass *
    feed.w_drymatter * feed.Elementary.myCl;
```

The water leaving the system is assumed to be pure. Unit: kg/kg

```
    cw1:          drain_water.Composition.AR = 0.0;
    cw2:          drain_water.Composition.C2H6 = 0.0;
    cw3:          drain_water.Composition.C3H8 =0.0;
    cw4:          drain_water.Composition.CH4 =0.0;
    cw5:          drain_water.Composition.CO =0.0;
    cw6:          drain_water.Composition.CO2 =0.0;
    cw7:          drain_water.Composition.H2 =0.0;
    cw8:          drain_water.Composition.H2O=0.0;
    cw9:          drain_water.Composition.H2S =0.0;
    cw10:         drain_water.Composition.N2 =0.0;
    cw11:         drain_water.Composition.O2 =0.0;
    cw12:         drain_water.Composition.SO2 =0.0;
```

The specific volume and heat capacity of the drain elementary have to be speficied. Units: $m^3$/kg and kJ/kgK

```
    ifl           ref(feed.Elementary) && ref(drain_sludge.Elementary) then
    v1:           feed.Elementary.v = drain_sludge.Elementary.v;
    elsel
    v2:           drain_sludge.Elementary.v = 1.0;
    endifl
    ifl           ref(feed.Elementary) && ref(drain_sludge.Elementary) then
    cp1:          feed.Elementary.cp = drain_sludge.Elementary.cp;
    elsel
    cp2:          drain_sludge.Elementary.cp = 1.0;
    endifl
```

The moisture content of the sludge can be direcly set as a variable. Unit: kg/kg

```
    slm:          sludge_moisture = drain_sludge.w_water;
```

Carbon in the feed is converted to CO2 according to aerobic metabolism. Unit: kg/s

```
    fco2:         CO2_formed = feed.mass * feed.w_drymatter * feed.Elementary.myC * conversion * 44/12;
```

The stoichiometric demand of oxygen for a set conversion is caluclated. Unit: kg/s

```
    f02:          O2_demand = (feed.mass * feed.w_drymatter * feed.Elementary.myH * 16 /2 + feed.mass *
    feed.w_drymatter * feed.Elementary.myC * 32/12 - feed.mass * feed.w_drymatter * feed.Elementary.myO) *
    conversion;
```

## Pressure and temperature balances.

No energy (heat) balance is calculated. Units: bar and °C

```
    pb1:          drain_sludge.p = 1.013;
    pb1a:         drain_water.p =1.013;
    pb2:          1.013 = feed.p - dp_feed;
    t1:           feed.t - dt_feed = t;
    t3:           drain_water.t = t;
    t5:           drain_sludge.t = t;
```

Pressure balance. The pressure in the air feed is calculated. Excess amount of oxygen (in percent) can be calculated or set, based on the demand of oxygen and the oxygen fed to the sytem. Unit: bar

```
    ifl           ref(feed_air) then
    pb4:          1.013 = feed_air.p - dp_air;
    mbair:        (feed_air.mass * feed_air.Composition.O2 - O2_demand ) * 100= excess_O2 * O2_demand;
    elsel
    mbair2:       excess_O2 =0.0;
    endifl
```

## Dimensions, pressure drop of air feed, stirrer input

The volume of the basin is calculated based on hydraulic retention time and massflows. Unit: $m^3$

```
    fvol:         feed.mass * feed.v * HRT* 3600 *24 = volume;
```

The minium pressure drop of air due to hydraulic pressure is calculated. Unit: Pa.

```
    fd:           dp_air * 1e5 = 1/drain_water.v * 9.81 * depth;
```

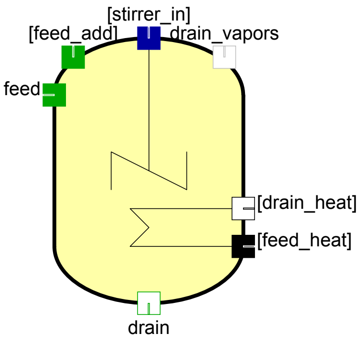
Power input via a stirrer. Unit: kW

```
ifl             ref(power_in) then
power1:         power_in.power = volume * spec_power_in /1000;
endifl
```

## Test section

```
ifl             !ref(feed.Elementary) || !ref(drain_sludge.Elementary) then
telementary:    test (0!=0)             error "Use use elementary objects in feed and drain_sludge ";
endifl
```

## *BF_BIOREACTOR, SUBMODEL BF_YEAST_PROPAGATION – NEW UNIT*



## DESCRIPTION

A model for the aerobic cultivation of yeast according to the equations (11) and (12) (see section 2.3).Only monomeric C6 sugars are converted to yeast biomass (ch_bact, p_bact and l_bact) and the respiration products $H_2O$ and $CO_2$. The formation of the by-products acetic acid and glycerol is accounted for. The nutrient demand can be derived from an elementary balance. For simplicity reasons, the ratio of the prodcuts $H_2O$ and $CO_2$ and the by-products is kept constant. All drymatter must be speficied by weender global objects.

## CONNECTORS

| | |
|---|---|
| vapors: | drain_vapors |
| bio_stream: | feed |
| bio_stream: | drain |
| bio_stream: | feed_add (optional) |
| shaft: | stirrer_in (optional) |
| stream: | feed_heat (optional) |
| stream: | drain_heat (optional) |

## VARIABLES AND PARAMETERS

| | | |
|---|---|---|
| spec_power_supply | Power of stirrer per $m^3$ of reactor volume (parameter) | [kW/$m^3$] |
| conv_to_biomass | Amount of C6 sugar converted to yeast biomass | [%] |
| conv_to_products | Amount of C6 sugar converted to products (H2O, CO2, acetic acid and glycerol) | [%] |
| stoich_O_demand | Stoichiometric demand of oxygen for chemical reactions | [kmol/s] |
| stoich_N_demand | Stoichiometric demand of nitrogen for chemical reactions | [kmol/s] |
| stoich_H_demand | Stoichiometric demand of hydrogen for chemical reactions | [kmol/s] |
| C_moles_available | Moles of Carbon available for microbbial conversion | [kmol/s] |
| final_yeast_conc | Final concentration of yeast in the ferementor (bach or fed-batch operation) | [g/l] |
| delta_p_htex | Pressure drop in the heat exchanger | [bar] |
| operating_p | Operating pressure | [bar] |
| operating_t | Operating temperature | [°C] |
| volume | Reactor volume | [$m^3$] |
| time | Hydraulic retention time in the fermentor | [h] |
| q_trans | Heat that has to be exchanged via the heat exchangers | [kW] |
| N_input | Input of Nitrogen that can be used by microorganism | [kg/s] |

## EQUATIONS

Depending on wheter the feed_add is connected and Biofuel globals are referenced in the feed, four cases have to be distinguished. For simplicity reasons, in this documentation only case 1a is explained. In this case i) the feed_add connector is not used and ii) no bioufel global is referenced in the feed. The other cases (1b, 2a, 2b) can be explored by opening the library in IPSEpros model development kit (MDK).

## Specific section for case 1a

```
ifl            !ref(feed_add) && (!ref(feed.Biofuel)&&ref(drain.Biofuel)) then
```

### The overall mass balance for case 1a

The demand of elements N, O and H is calculated. Elements H and O are supplied by water. N has to be supplied externally. Unit: kg/s

```
omb1a:         feed.mass + stoich_N_demand + stoich_O_demand + stoich_H_demand = drain.mass +
drain_vapors.mass;
```

The amount of moles or carbon in the feed is calculated. This quantity defines the amount of substrate that can be convertedto products in the reactor and is used in all chemical reactions. Unit: kmol/s

```
cmol1a:        C_moles_available = feed.mass* feed.w_drymatter* feed.Weender.CH_mono_C6* 6/180;
```

### The mass balance for stream components

The mass balance of stream component water. In the steady state assumed, ingoing streams + sources (chemical reactions) are equal to outgoing streams +sinks (chemical reactions). Unit: kg/s

```
mbw1a:         drain.mass * drain.w_water + drain_vapors.mass * drain_vapors.w_water + C_moles_available*
conv_to_products * 0.02 * 1/3 * 18 = feed.mass * feed.w_water + C_moles_available * conv_to_products *(1-0.06)
*18;
```

The mass balance of stream component composition (CO2). Unit: kg/s

```
mbco1a:        drain.mass * drain.w_composition + drain_vapors.mass * drain_vapors.w_composition
= feed.mass * feed.w_composition + C_moles_available * conv_to_products * (1- 0.06) * 44;
```

The mass balance of stream componet biofuel is ommited, instead the full set of biofuel species is given. Ethanol balance. No ethanol is formed. Unit: kg/s

```
mbbfe1a:       drain.mass * drain.w_biofuel * drain.Biofuel.etoh = feed.mass * feed.w_biofuel;
```

### The biofuel species balance

Glycerol balance. Glycerol is formed according to the factor conv_to_biomass. It is assumed that of the substrate that is converted, 2% are converted to glycerol. Unit: kg/s

```
mbbfg1a:       drain.mass * drain.w_biofuel * drain.Biofuel.glycerol = C_moles_available * conv_to_products * 0.02
* 92 *1/3;
```

Acetic acid balance. Acetic acid is formed according to the factor conv_to_biomass. It is assumed that of the substrate that is converted, 4% are converted to acetic acid. Unit: kg/s

```
mbbfh1a:       drain.mass * drain.w_biofuel * drain.Biofuel.acetic_acid = C_moles_available * conv_to_products *
0.04 * 60 *1/2;
```

Furfural balance. No furfual is formed. Unit: kg/s

```
mbbff1a:       drain.mass * drain.w_biofuel * drain.Biofuel.furfural = 0;
```

### The weender species balance

A part of drymatter (monomeric C6 sugars) are converted to yeast. However, the explicit balance for monomeric C6 sugars (CH_mono_C6) is omitted. Yeast is composed of 40w/w% carbohydrate (CH_bact), 55w/w% protein (P_bact) and 5w/w% fats (L_bact). All other species pass the system unconverted. Unit: kg/s

```
w1a1a:         drain.mass * drain.w_drymatter * drain.Weender.CH_bact
= feed.mass * feed.w_drymatter * feed.Weender.CH_bact + 0.4 * 24.737 * conv_to_biomass * C_moles_available;
w1b1a:         drain.mass * drain.w_drymatter * drain.Weender.P_bact_int
= feed.mass * feed.w_drymatter * feed.Weender.P_bact_int + 0.55 * 24.737 * conv_to_biomass *
C_moles_available;
w1c1a:         drain.mass * drain.w_drymatter * drain.Weender.L_bact
= feed.mass * feed.w_drymatter * feed.Weender.L_bact + 0.05 * 24.737 * conv_to_biomass * C_moles_available;
w21a:          drain.mass * drain.w_drymatter * drain.Weender.CH_starch
= feed.mass * feed.w_drymatter * feed.Weender.CH_starch;
 w41a:         drain.mass * drain.w_drymatter * drain.Weender.CH_mono_C5
= feed.mass * feed.w_drymatter * feed.Weender.CH_mono_C5;
w51a:          drain.mass * drain.w_drymatter * drain.Weender.CH_cell
= feed.mass * feed.w_drymatter * feed.Weender.CH_cell;
w61a:          drain.mass * drain.w_drymatter * drain.Weender.CH_hemicell
= feed.mass * feed.w_drymatter * feed.Weender.CH_hemicell;
w71a:          drain.mass * drain.w_drymatter * drain.Weender.CH_lignin
=feed.mass * feed.w_drymatter * feed.Weender.CH_lignin;
w81a:          drain.mass*drain.w_drymatter * drain.Weender.P_bact_ext
=feed.mass * feed.w_drymatter * feed.Weender.P_bact_ext;
```

```
w91a:         drain.mass*drain.w_drymatter * drain.Weender.P_plant
= feed.mass * feed.w_drymatter * feed.Weender.P_plant;
w101a:        drain.mass*drain.w_drymatter * drain.Weender.L_fats
= feed.mass * feed.w_drymatter * feed.Weender.L_fats;
w111a:        drain.mass * drain.w_drymatter * drain.Weender.ash
    = feed.mass * feed.w_drymatter * feed.Weender.ash;
```

## Energy balance and reaction volume

The energy leaving the system via product streams (drain and vapors) equals to the heat that is fed to the system via incoming stream (feed) + the heat that is released through chemical reactions + the heat that is exchanged in the heat exchangers + heat induced via stirring. Heat of reaction is assumed to be 1000 kJ/mol glucose consumed (1000000 kJ/kmol). The enthalpy of vaporization of CO2 is included. Unit: kW

```
eb1a:         drain.mass * drain.h + drain_vapors.mass * drain_vapors.h = feed.mass * feed.h + q_trans +
C_moles_available * ( conv_to_products + conv_to_biomass ) * 1/6 * 1000000 + spec_power_supply * volume
+ C_moles_available * conv_to_products * 44 * 348.24;
```

The reaction or reactor volume is calculated based on the mass flow and the residence time. Unit: $m^3$

```
vol1a:        volume = feed.mass * feed.v * time * 3600;
```

Here the specfic section for case 1a ends. The cases 1b, 2a and 2b are not listed here (as indicated by the dots), but can be examined in the library using IPSEpro's MDK.

```
endifl
```

## Specific section for case 1b, 2a, 2b are not included

```
ifl           ref(feed_add) && (!ref(feed.Biofuel)&&ref(drain.Biofuel)) then
….
endifl
ifl           !ref(feed_add) && (ref(feed.Biofuel)&&ref(drain.Biofuel)) then
….
endifl
ifl           ref(feed_add) && (ref(feed.Biofuel)&&ref(drain.Biofuel)) then
….
endifl
```

## The general section

Here, the general section starts with the calculation of Nitrogen, Oxygen and Hydrogen demand. These quantities are used in the overall mass balance and are for a correct elementary balance. Typically, the hydrogen demand will be very close to 0, only a numerical uncertainty is remains. The nitrogen demand and the oxgyven demand are unequal to zero and can be used to calculated the necessary amount of nutrients and air, repsectively. Generally, the equations have the form: element demand = elemnt in product – element input. However, the nitrogen input is not considered because nitrogen may not be available for the microorganisms. Instead the Nitrogen input is calculated sepearately. Unit: kg/s

## Elementary balance and yeast concentration

```
oxd1:         stoich_O_demand = C_moles_available * (conv_to_products * (1- 0.06) * 1 * 32+ conv_to_biomass
* (0.557 -1) * 16  conv_to_products * (0.02) * 1/6 * 32 );
nd1:          stoich_N_demand = C_moles_available * (conv_to_biomass * 0.158) * 14;
hd1:          stoich_H_demand = C_moles_available * (conv_to_biomass * 1.613 + conv_to_products * 2)*1 -
C_moles_available * (conv_to_biomass +conv_to_products)*1*2;
```

The nitrogen Input is calculated separately. Cases wheter feed_add is connected or not have to be distinguished. Units: kg/s

```
ifl           !ref(feed_add) then
nin1:         N_input = feed.mass * feed.w_drymatter * (feed.Weender.P_bact_int + feed.Weender.P_bact_ext +
feed.Weender.P_plant ) * 0.173;
endifl
ifl           ref(feed_add) then
nin2:         N_input = (feed.mass* feed.w_drymatter * (feed.Weender.P_bact_int + feed.Weender.P_bact_ext +
feed.Weender.P_plant ) + (feed_add.mass * feed_add.w_drymatter * (feed_add.Weender.P_bact_int +
feed_add.Weender.P_bact_ext + feed_add.Weender.P_plant))) * 0.173;
endifl
```

The final concentration of yeast in the batch in calucated. It is assumed that no other microorganisms (MO) or MO-components (CH_bact, P_bact, L_bact) enter the reactor. If this is the case, this concentration value is wrong! Unit: g/l

```
y1:           final_yeast_conc = drain.w_drymatter * (drain.Weender.P_bact_int + drain.Weender.CH_bact +
drain.Weender.L_bact)/drain.v;
```

## Pressure balance, stirrer, heat exchangers

Assumptions regarding the pressures and temperatures. Units: bar and °C.

```
pb1:          operating_p = drain.p;
pb2:          operating_p = drain_vapors.p;
eb1:          operating_t = drain_vapors.t;
```

```
    eb2:            operating_t = drain.t;
```

The power input via stirring. Only applies if the stirrer is connected. Unit: kW.

```
    ifl             ref(stirrer_in) then
    pw1:            stirrer_in.power = spec_power_supply * volume;
    endifl
```

The mass, energy and pressure balances for the heat exchanger. Only apply, if the heat exchanger is connected. Units: kg/s, bar, kW.

```
    ifl             ref(drain_heat) && ref(feed_heat) then
    mbh:            feed_heat.mass = drain_heat.mass;
    ebh:            drain_heat.mass * drain_heat.h + q_trans = feed_heat.mass * feed_heat.h;
    pbh:            drain_heat.p + delta_p_htex = feed_heat.p;
    endifl
```

## The vapour liquid equilibrium

The respective amounts of $CO_2$ and water are in the product stream. The solubility of CO2 in water is calculated using Henry's law. Dimension of Henry's constant is bar * mol/mol. Unit: bar

```
    mbcd:           drain.w_composition / 44 / (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel / 46 ) *
    fhenry_co2_water1(drain_vapors.t) = drain_vapors.p * drain_vapors.w_composition / 44 /
    (drain_vapors.w_composition / 44 + drain_vapors.w_water / 18 + drain_vapors.w_biofuel / 46 );
```

The amount of water in the drain vapors is calculated according to Raoult's law. Unit: bar

```
    mbwv:           drain_vapors.p * drain_vapors.w_water / 18 / (drain_vapors.w_composition / 44 +
    drain_vapors.w_water / 18 + drain_vapors.w_biofuel / 46 ) = fptx_h2o(drain_vapors.t) *  drain.w_water / 18 /
    (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel / 46);
```

It is assumed that no other volatiles are recovered in the vapours. A simplification. Unit: kg/kg

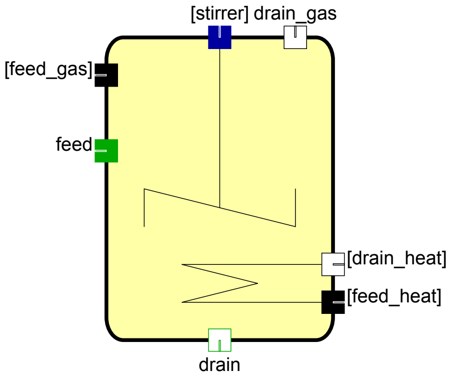
```
    mbetvap:                drain_vapors.w_biofuel = 0;
```

## The test section

Checks for correct setup of globals and conversion >1.

```
    ifl             ref(feed_add.Biofuel) then
    tbiofuel01:     test (0!=0)                 error "Dont use biofuel global in feed_add ";
    endifl
    ifl             ref(drain_vapors.Biofuel) then
    tbiofuel02:     test (0!=0)                 error "Dont use biofuel global in drain vapors ";
    endifl
    ifl ref(feed.Biofuel)==ref(drain.Biofuel) then
    tbiofuel03:     test (0!=0)                 error "Dont use same biofuel global in feed and drain ";
    endifl
    t1:             test (conv_to_products+conv_to_biomass <= 1.0)          error "Sum of conversions >= 1.0";
    ifl             (!ref(feed.Weender) || !ref(drain.Weender)) then
    tweender:       test (0!=0)                 error "Use weender global objects in feed and drain! ";
    endifl
```

### *BF_CH4_FERMENTER, SUBMODEL: BF_CH4_FERMENTER_PROD – MODIFICATIONS*



## CONNECTORS

stream: drain_gas
bio_stream: feed
bio_stream: drain
stream: feed_heat (optional)
stream: drain_heat (optional)
stream: feed_gas (optional)
shaft: stirrer (optional)

## DESCRIPTION

A model for the anaerobic digestion of biomass. In this work only the submodel bf_ch4_fermenter_prod is used. Biomass is converted according to a modified version of the Buswell equation (13) (see section 2.3). Production factors for CH4 and CO2 are used to decouple the formation of these species. Organic dry matter entering the reactor must be specified as elementary global object. Likewise, the drain is specified by an elementary object. In addition to the Buswell equation, formation of H2S from sulfur in the feed is considered. The production factors define to which extent CO2 and CH4 are formed. Within this work, the existing model was extended by a set of parameters regarding the chemical oxygen demand (COD). In addition the commonly used performance paratmeres organic loading rate (OLR) and productivity were introduced. The new variables are shown in bold. In addition two variables were renamed (gas_yield and methane_yield). Now the more commonly used names are introduced.

## VARIABLES & PARAMETERS

| | | |
|---|---|---|
| n | Stoichiometric coefficient for C acc. to Buswell formula | [kmol/s] |
| a | Stoichiometric coefficient for H acc. to Buswell formula | [kmol/s] |
| b | Stoichiometric coefficient for O acc. to Buswell formula | [kmol/s] |
| **c** | **Stoichiometric coefficient for N acc. to definition of COD** | **[kmol/s]** |
| prod_CH4 | Production factor CH4, fraction of maximum CH4 production acc. to Buswell Formula | [-] |
| prod_CO2 | Production factor CO2, fraction of maximum CO2 production acc. to Buswell Formula | [-] |
| residual_S | Fraction of S that is not converted to H2S | [-] |
| delta_p_htex | Pressure drop heat exchanger | [bar] |
| operating_p | Operating pressure | [bar] |
| operating_t | Operating temperature | [°C] |
| residence_time | Hydraulic residence time | [d] |
| q_trans | Transferred heat | [kW] |
| spec_power | Specific power input stirrer | [kW/m³] |
| mash_volume | Volume mash | [m³] |
| gas_per_day | Gas yield per day | [Nm³/d] |
| **gas_yield** | (old name: gas_efficiency_tot) Total gas yield per kg volatile solids | [Nm³/kg] |
| **methane_yield** | (old name: gas_efficiency_CH4) Total methane yield per kg volatile solids | [Nm³/kg] |
| **CH4_productivity** | **Productivity of methane** | **[Nm³/m³d]** |
| **COD_feed_c** | **Concentration of chemical oxygen demand in the feed** | **[g /l]** |
| **COD_feed_m** | **Massf flow of chemical oxygen demand in the feed** | **[kg/s]** |
| **COD_drain_m** | **Massflow of chemical oxygen demand in the drain** | **[kg/s]** |
| **OLR_cod** | **Organic loading rate COD** | **[kg/m³d]** |
| **OLR_vs** | **Organic loading rate volatile solids** | **[kg/m³d]** |
| **COD_removal** | **Percentage of COD removed in the fermenter** | **[%]** |

## NEW EQUATIONS

In this section only new equations are shown. First, the stoichiometric coefficients are defined. Here the new variable c, the stoichiometric coefficient for Nitrogen was introduced. Units: kmol/s

fc: c = feed.mass * feed.w_drymatter * feed.Elementary.myN / 14.0067;

The chemical oxygen demand (COD) of the feed is calculated in terms of massflow. Units kg/s.

fcod: COD_feed_m = (n + a/4 - b/2 -3/4*c) * 15.9994*2;

and as concentration. Unit: g/l.

fcod2: COD_feed_c = COD_feed_m / (feed.mass * feed.v);

moreover, the COD in the drain is calculated as massflow. Unit: kg/s.

fcod3: COD_drain_m = drain.mass * drain.w_drymatter * (drain.Elementary.myC / 12.011 + drain.Elementary.myH / 1.00794 / 4 - drain.Elementary.myO / 15.9994 / 2 - drain.Elementary.myN / 14.0067 * 3 /4 ) * 15.9994*2;

The removal of COD is calculated bases on the COD entering and leaving the system. Unit: %.

fcod4: COD_removal = (1- COD_drain_m / COD_feed_m)*100;

The performance parameter organic loading rate (OLR) is introduced. Here it is defined as the amount of COD that enters the fermenter in one day divided by the fermenter size. Unit: kg/m³d.

olr: OLR_cod = COD_feed_m *3600 * 24 / mash_volume;

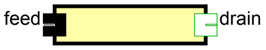
The OLR can also be expressed in terms of volatile solids. Unit: kg/m$^3$d.

```
olr2:           OLR_vs = feed.mass * feed.w_drymatter * (1 - feed.Elementary.myAsh) *3600 *24 /mash_volume;
```

The methane productivity is calculated. Unit: m$^3$/m$^3$d.

```
fprod:          CH4_productivity = drain_gas.mass * drain_gas.Composition.CH4 * fv(1.01325, 1.0, 0.0, 0.0, 0.0,
0.0, 1.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0) * 24 * 3600 / mash_volume;
```

## *BF_CONVERTER – NEW UNIT*



### CONNECTORS

bio_stream: drain
stream: feed

### DESCRIPTION

This is a simple model that has no physical meaning. However, it can be usefull for flowsheet modeling. A stream that references a compoisiton global that only contains water (like it is used in steam cylces) is converted to a bio_stream that contains only water.

### VARIABLES

There are no variables in this model.

### EQUATIONS

The mass is conserved. Unit: kg/s.

```
mb:             feed.mass = drain.mass;
```

The temperature or energy and the pressure are conserved. Unit: °C or kJ and bar.

```
ft:             if   isconverged(feed.t) then
drain.t = feed.t;
                else
feed.h = drain.h;
pb:             feed.p = drain.p;
```

All other biostream components in the drain are set to zero.

```
bf:             drain.w_biofuel =0;
c:              drain.w_composition = 0;
dm:             drain.w_drymatter =0;
```

Test section. The composition global in the feed must contain only water.

```
t1:             test (feed.Composition.WATER >= 1.0)            error "Connect only WATER to feed! ";
```

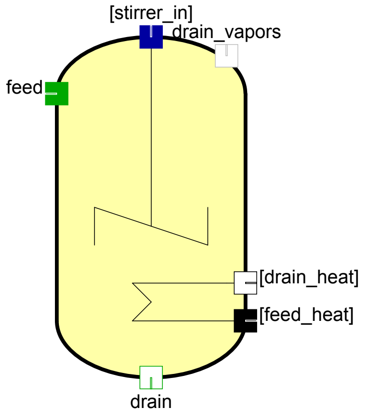
The mass fraction of water in drain must

```
t2:             test(drain.w_water >=1.0 )                      error "w_water in drain < 1  ";
```

No weender, elementary or biofuel globals must be referenced in the drain.

```
ifl     (ref(drain.Weender) || ref(drain.Elementary) || ref(drain.Biofuel))
                then
t3:             test (0!=0)            error "Dont use Weender, Elementary or Biofuel Global in Drain";
                endifl
```

## *BF_ENZYMEPRODUCTION – NEW UNIT*



### Connectors

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain |
| vapors: | drain_vapors |
| stream: | feed_heat (optional) |
| stream: | drain_heat (optional) |
| shaft: | stirrer_in (optional) |

### Description

A model for the production of cellulase enzymes according to equation (10). In addition to enzyme production, aerobic metabolism takes place (11) and trichoderm biomass is formed (12) (see section 2.3). In contrast to yeast, Trichoderma can utilize all monomeric and polymeric carbohydrates for its metabolism (CH_cell, CH_mono_C6, CH_mono_C5, CH_starch, CH_hemicell). Accordingly, the amount of carbon available is caluclated (C_moles_available). For simplicity reasons, it is assumed that all carbohydrates are converted with the same factor.

### Variables & Parameters

| | | |
|---|---|---|
| spec_power_supply | Power of stirrer per m³ of reactor volume (parameter) | [kW/m³] |
| conv_to_enzym | Amount of substrate converted to cellulase enzyme | [%] |
| conv_to_biomass | Amount of substrate converted to biomass | [%] |
| conv_to_CO2 | Amount of substrate converted to CO2 | [%] |
| stoich_O_demand | Stoichiometric demand of oxygen | [kg/s] |
| stoich_N_demand | Stoichiometric demand of nitrogen | [kg/s] |
| stoich_H_demand | Stoichiometric demand of hydrogen | [kg/s] |
| N_input | Input of nitrogen via substrate | [kg/s] |
| C_moles_available | Moles of Carbon available for microbbial metabolism | [kmol/s] |
| Yxs | Biomass yield | [kg/kg] |
| Yes | Enzyme yield | [kg/kg] |
| final_enzyme_conc | Final concentration of enzyme in the production | [g/l] |
| delta_p_htex | Pressure drop heat exchanger | [bar] |
| operating_p | Operating pressure | [bar] |
| operating_t | Operating temperature | [°C] |
| volume | Reactor volume | [m³] |
| time | Residence time in bioreactor | [h] |
| q_trans | Heat transferred between reactor and heat exchanger | [kW] |

### Equations

#### General mass balance

Overall mass balance. Just as in yeast production, the stoichiometric demand for Oxygen, Nitrogen and Hydrogen have to be considered, so that the elementary balance is correct. Unit: kg/s

mboa: drain.mass + drain_vapors.mass = feed.mass + stoich_O_demand + stoich_N_demand + stoich_H_demand;

The amount of carbon (in moles) is calculated. This variable is speficies the part of the substrate that is availbale for bioreactions. In contrast to yeast propagation all carbohydrates can be converted to products. Unit: kmol/s

```
mbcmoles:       C_moles_available = feed.mass * feed.w_drymatter * ((feed.Weender.CH_cell +
feed.Weender.CH_starch)* 6 / 162 + feed.Weender.CH_mono_C5 * 5 / 150 + feed.Weender.CH_mono_C6 * 6 /
180 + feed.Weender.CH_hemicell * 5 / 132);
```

## Elementary balance

These quantities are used in the overall mass balance and are necessary for a correct elementary balance. Typically, the hydrogen demand will be very close to 0, only a numerical uncertainty is remains. The nitrogen demand and the oxgyven demand are unequal to zero and can be used to calculate the necessary amount of nutrients and air, repsectively. Generally, the equations have the form:

element demand = elemnt in products – element input.

However, the nitrogen input is not considered because nitrogen may not be available for the microorganisms. Instead the Nitrogen input is calculate as separate variable.Unit: kg/s

The oxygen demand is calculated as the amount of oxygen that is fed to the sytem via cellulose and starch (in kmol/s)…

```
oxd1:               stoich_O_demand = feed.mass * feed.w_drymatter * (( feed.Weender.CH_cell +
feed.Weender.CH_starch)* 6 / 162 *
```

and is converted to oxygen in enzyme (oxygen content in protein 0.323 mol/mol), trichoderma biomass (O-content 0.557), CO2 and H2O.

```
(conv_to_enzym * 0.323  + conv_to_biomass* 0.557 + conv_to_CO2 * (2 + 5/6))
```

+ the amount of oxygen in hemicellulose (kmol/s)…

```
+ (feed.Weender.CH_hemicell * 5 / 132)
```

that is converted to the products enzym, biomass, CO2 and water…

```
* (conv_to_enzym * 0.323 + conv_to_biomass* 0.557 + conv_to_CO2 * (2 + 4/5))
```

+ the amount of oxygen in monomeric sugars (kmol/s)…

```
+ (feed.Weender.CH_mono_C5 / 150* 5 + feed.Weender.CH_mono_C6 / 180 * 6)
```

that is converted to the products enzym, biomass, CO2 and water…

```
* (conv_to_enzym * 0.323 + conv_to_biomass* 0.557 + conv_to_CO2 * (2 + 1)))
```

times the molar mass of oxygen (kg/kmol)

```
* 16
```

The oxygen input that is converted, is calulaced and subtracted from the amount that is stored in the products to obtain the oxygen demand.

```
- feed.mass * feed.w_drymatter * ((feed.Weender.CH_cell + feed.Weender.CH_starch) / 162 * 5 +
feed.Weender.CH_mono_C5 / 150 * 5 + feed.Weender.CH_mono_C6 / 180 * 6 + feed.Weender.CH_hemicell * 4
/132) * 16 * (conv_to_enzym + conv_to_biomass +conv_to_CO2);
```

The stoichiometric hydrogen demand is calculated in the same way as the oxygen demand. 1.588 and 1.613: hydrogen content in enzyme and biomass. Unit: kg/s

```
hd1:                stoich_H_demand = feed.mass * feed.w_drymatter * ((feed.Weender.CH_cell +
feed.Weender.CH_starch)* 6 / 162
*(conv_to_enzym * 1.588+ conv_to_biomass* 1.613 + conv_to_CO2 * 2* ( 5/6))
+ (feed.Weender.CH_hemicell * 5/ 132 )
* (conv_to_enzym * 1.588 + conv_to_biomass* 1.613 + conv_to_CO2 * 2* (4/5))
+(feed.Weender.CH_mono_C5 / 150 * 5 + feed.Weender.CH_mono_C6 / 180 * 6)
* (conv_to_enzym * 1.588 + conv_to_biomass * 1.613 + conv_to_CO2 * 2*(1)))
*1
- feed.mass * feed.w_drymatter * ((feed.Weender.CH_cell + feed.Weender.CH_starch) / 162 * 10 +
feed.Weender.CH_mono_C5 / 150 * 10 + feed.Weender.CH_mono_C6 / 180 * 12 + feed.Weender.CH_hemicell * 8
/132) * 1 * (conv_to_enzym + conv_to_biomass +conv_to_CO2);
```

The nitrogen demand is calculated only as the nitrogen stored in products (microbial biomass and enzyme) Unit: kg/s

```
nd1:                stoich_N_demand =  feed.mass * feed.w_drymatter * ((feed.Weender.CH_cell +
feed.Weender.CH_starch)* 6 / 162  + feed.Weender.CH_mono_C5 * 5 / 150 + feed.Weender.CH_mono_C6 * 6 /
180 + feed.Weender.CH_hemicell * 5 / 132) * (conv_to_enzym * 0.280 + conv_to_biomass* 0.158) *14;
```

The input of nitrogen through the substrate is calculated. The nitrogen content of protein is assumed to be 0.173 g/g. This value can be used to calculate the nutrient demand. Unit: kg/s

```
nin1:               N_input = feed.mass* feed.w_drymatter*(feed.Weender.P_bact_int + feed.Weender.P_bact_ext
+feed.Weender.P_plant)*0.173;
```

## The mass balance for the stream components

The drymatter balance is omitted. Water is formed through the areobic consumption of carboydrates and cosumed by hydrolysis of polymeric carbohydrates. Unit: kg/s

```
mbwa:               drain.mass * drain.w_water + drain_vapors.mass * drain_vapors.w_water = feed.mass *
feed.w_water
```

Water formed trough aerobic consumption of carbohydrates (1 mole water per mole CO2, 18 kg/kmol water)

```
+ C_moles_available * ( conv_to_CO2 * 1* 18 )
```

Water is consumed in the hydrolysis of starch, cellulose and hemicellulose

```
	- feed.mass * feed.w_drymatter * (feed.Weender.CH_cell + feed.Weender.CH_starch)* 6 / 162 * ( conv_to_CO2 *
	1/6 * 18 ) - feed.mass * feed.w_drymatter * feed.Weender.CH_hemicell * 5 / 132 * ( conv_to_CO2 * 1/5* 18 );
```

Biofuel blanance. No biofuel is formed and all biofuel species fed to the system leave it in the drain. Unit: kg/s

```
	mbbfa:		drain.mass * drain.w_biofuel = feed.mass * feed.w_biofuel;
```

Balance for CO2. CO2 is formed when carbohydrates are consumed aerobically.

```
	mbca:		drain_vapors.mass * drain_vapors.w_composition + drain.mass * drain.w_composition = feed.mass
	* feed.w_composition + C_moles_available * ( conv_to_CO2 * 44 );
```

## The balance for the weender species in the drymatter

Trichoderma biomass (CH_bact, P_bact_int, L_bact) and cellulase enzymes (P_bact_ext) are formed from the carbohydrates. The variable C_moles_available and the respective conversions are used. Unit: kg/s

Formation of cell mass. It is assumed that cell mass has a molar mas of 24.737 g/mol and the following composition: 40% Carbohydrate, 55% Protein, 5% Fat.

```
	w1:		drain.mass * drain.w_drymatter * drain.Weender.CH_bact= feed.mass * feed.w_drymatter *
	feed.Weender.CH_bact + 0.4 * 24.737 * conv_to_biomass * C_moles_available;
	w7a:		drain.mass * drain.w_drymatter * drain.Weender.P_bact_int = feed.mass * feed.w_drymatter *
	feed.Weender.P_bact_int + 0.55 * 24.737 * conv_to_biomass * C_moles_available;
	w9:		drain.mass * drain.w_drymatter * drain.Weender.L_bact = feed.mass * feed.w_drymatter *
	feed.Weender.L_bact + 0.05 * 24.737 * conv_to_biomass * C_moles_available;
```

Conversion of carbohydrates

```
	w2:		drain.mass * drain.w_drymatter * drain.Weender.CH_starch = feed.mass * feed.w_drymatter *
	feed.Weender.CH_starch * (1-(conv_to_enzym + conv_to_biomass + conv_to_CO2));
	w3a:		drain.mass * drain.w_drymatter * drain.Weender.CH_mono_C6 = feed.mass * feed.w_drymatter *
	feed.Weender.CH_mono_C6*  (1-(conv_to_enzym + conv_to_biomass + conv_to_CO2));
	w3:		drain.mass * drain.w_drymatter * drain.Weender.CH_mono_C5 =feed.mass * feed.w_drymatter *
	feed.Weender.CH_mono_C5 * (1-(conv_to_enzym + conv_to_biomass + conv_to_CO2));
	w4:		drain.mass * drain.w_drymatter * drain.Weender.CH_cell = feed.mass * feed.w_drymatter *
	feed.Weender.CH_cell * (1-(conv_to_enzym + conv_to_biomass + conv_to_CO2));
	w5:		drain.mass * drain.w_drymatter * drain.Weender.CH_hemicell = feed.mass * feed.w_drymatter *
	feed.Weender.CH_hemicell * (1-(conv_to_enzym + conv_to_biomass + conv_to_CO2));
```

Lingin, extractives and protein are not not converted…

```
	w6:		drain.mass * drain.w_drymatter * drain.Weender.CH_lignin = feed.mass * feed.w_drymatter *
	feed.Weender.CH_lignin;
	w8:		drain.mass * drain.w_drymatter * drain.Weender.P_plant = feed.mass * feed.w_drymatter *
	feed.Weender.P_plant;
	w10:		drain.mass * drain.w_drymatter * drain.Weender.L_fats = feed.mass * feed.w_drymatter *
	feed.Weender.L_fats;
```

Formation of cellulase enzyme. The molar mass is assumed to be 22.676 kg/koml.

```
	w7:		drain.mass * drain.w_drymatter * drain.Weender.P_bact_ext = feed.mass * feed.w_drymatter *
	feed.Weender.P_bact_ext + 22.676 * conv_to_enzym * C_moles_available;
```

The ash balance is omitted.

## Yield calculation & Enzyme concentration

The biomass yield and the enzyme yield are calculated. Units: kg/kg

```
	yxs:		Yxs = (drain.mass * drain.w_drymatter * drain.Weender.CH_bact/0.4-feed.mass * feed.w_drymatter
	* feed.Weender.CH_bact/0.4)/(feed.mass* feed.w_drymatter* (feed.Weender.CH_mono_C5 +
	feed.Weender.CH_mono_C6 +feed.Weender.CH_cell +feed.Weender.CH_hemicell));
	yes:		Yes = (drain.mass * drain.w_drymatter * drain.Weender.P_bact_ext)/(feed.mass* feed.w_drymatter*
	(feed.Weender.CH_mono_C5 + feed.Weender.CH_mono_C6 +feed.Weender.CH_cell +
	feed.Weender.CH_hemicell));
```

The concentration of enzyme at the end of enzyme production is calculated. Unit: g/l

```
	ec1:		final_enzyme_conc = drain.w_drymatter * (drain.Weender.P_bact_ext)/drain.v;
```

## Energy balance and temperature assumptions

The temperature in the drain and drain_vapors is assumed to be identical to the temperature in the reactor. Unit: °C

```
	eb1:		operating_t = drain_vapors.t;
	eb2:		operating_t = drain.t;
```

In the energy balance the heat of reaction is considered and assumed to be 200 kJ/mol carbohydrate consumed. The enthalpy of vaporization of CO2 is included. Unit: kW

```
	eb3:		 drain.mass * drain.h + drain_vapors.mass * drain_vapors.h = feed.mass * feed.h + q_trans +
	C_moles_available * (conv_to_enzym + conv_to_biomass + conv_to_CO2) * 200000/6 + spec_power_supply *
	volume + C_moles_available * conv_to_CO2 * 44 * 348.24;
```

## Pressure balance, stirrer, reaction volume, heat exchanger balances

The reaction or reactor volume is calculated based on the mass flow and the residence time. Unit: $m^3$

```
	vol:		volume = feed.mass * feed.v * time * 3600;
```

The typical assumptions for pressures in the drain and drain_vapors. Unit: bar

```
    pb1:            operating_p = drain.p;
    pb2:            operating_p = drain_vapors.p;
```

Power requirement of the stirrer. Unit: kW

```
    ifl             ref(stirrer_in) then
    pw1:            stirrer_in.power = spec_power_supply * volume;
    endifl
```

Heat exchanger mass, energy and pressure balance. Units: kg/s, kW and bar.

```
    ifl             ref(drain_heat) && ref(feed_heat) then
    mbh:            drain_heat.mass = feed_heat.mass;
    ebh:            feed_heat.mass * feed_heat.h = q_trans + drain_heat.mass * drain_heat.h;
    pb3:            drain_heat.p + delta_p_htex = feed_heat.p;
    endifl
```

## Vapour liquid equilibrium

Through the VLE the composition of the drain_vapors (Raoult's law) and the amount of dissolved CO2 (Henry's law) in the drain are defined.

The partial pressure of water in the drain_vapors is calcualted according to Raoult's law. Unit: bar

```
    mbwv:           drain_vapors.p * drain_vapors.w_water / 18 / (drain_vapors.w_composition / 44 +
    drain_vapors.w_water / 18 + drain_vapors.w_biofuel / 46) = fptx_h2o(drain_vapors.t) * drain.w_water / 18  /
    (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel / 46 );
```

The CO2 solubilit is calculated using Henry's law. Unit: bar

```
    mbcd:           drain.w_composition/ 44 / (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel / 46 ) *
    fhenry_co2_water1(drain_vapors.t) = drain_vapors.p * drain_vapors.w_composition / 44 /
    (drain_vapors.w_composition / 44 + drain_vapors.w_water / 18 + drain_vapors.w_biofuel / 46 );
```

There is no biofuel in the drain_vapor. Unit: kg/kg

```
    mbetvap:                drain_vapors.w_biofuel = 0;
```

## Test section

The sum of conversions must be smaller than 1.

```
    t1:             test (conv_to_enzym+conv_to_biomass+conv_to_CO2 <= 1.0) error "Sum of conversions >= 1.0";
```

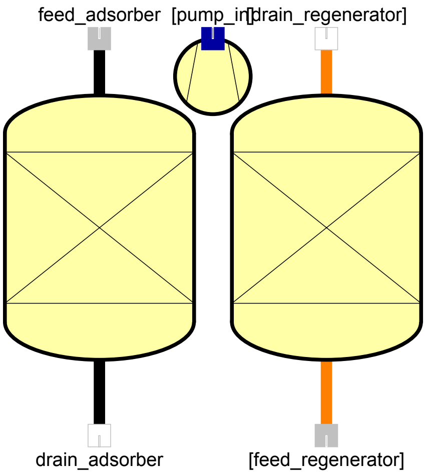
Check for correct setup of weender globals

```
    ifl             (!ref(feed.Weender) || !ref(drain.Weender))
    then
    tweender:       test (0!=0) error "Use weender global objects in feed and drain! ";
    endifl
```

Check for correct setup of biofuel globals

```
    ifl             (ref(feed.Biofuel)&&!ref(drain.Biofuel)) || (!ref(feed.Biofuel) && ref(drain.Biofuel)) ||
    (ref(feed.Biofuel)&&ref(drain.Biofuel)&&(ref(feed.Biofuel)!=ref(drain.Biofuel)))
    then
    tbiofuel02:     test (0!=0) error "Use same biofuel object in feed and drain! ";
    endifl
```

## *BF_ETOH_ADSORBER - MODIFICATIONS*



### CONNECTORS

vapors: feed_adsorber
vapors: drain_adsorber
vapors: feed_regenerator (optional)
vapors: drain_regenerator (optional)
shaft: pump_in (optional)

### DESCRIPTION

A simple black-box model for the pressure swing adsorption (PSA) unit that is used to remove water from a precontentrated ethanol stream. This model is steaty state whereas a real PSA unit works in cyclic batch mode. The previously existing unit was modified, however, since the new unit is relatively simple, the whole set of equations is presented here.

### VARIABLES

| | | |
|---|---|---|
| rem_eff_h2o | Removal efficiency of water | [%] |
| water_adsorbed | Water adsorbed in bed | [kg/s] |
| delta_p_adsorber | Pressure drop of the vapors | [bar] |
| delta_p_regenerator | Pressure difference in the regenerator | [bar] |
| spec_work | Specific work to operate compressors for production of 1 kg ethanol | [kJ/kg] |

### EQUATIONS

#### General mass balance and adsorption

The mass is conserved in the adsorber and the removal efficiency is defined. Units: kg/s

mbo: feed_adsorber.mass = drain_adsorber.mass + water_adsorbed ;
mb02: water_adsorbed = feed_adsorber.mass * feed_adsorber.w_water * rem_eff_h2o;

Also in the regenerator the mass is conserved. Water that was adsorbed in a previous cycle is removed from the regenerator. Unit: kg/s

ifl ref(feed_regenerator) && ref(drain_regenerator) then
mbr: drain_regenerator.mass = feed_regenerator.mass + water_adsorbed;
endifl

#### Species balance

The species balance for water in the adsorber. Unit: kg/s

mbw: drain_adsorber.mass * drain_adsorber.w_water = feed_adsorber.mass * feed_adsorber.w_water - water_adsorbed;

The species balance for composition in the adsorber. Unit: kg/s

mbc: drain_adsorber.mass * drain_adsorber.w_composition = feed_adsorber.mass* feed_adsorber.w_composition;

The biofuel (ethanol) species balance for the adsorber is omitted.

The species balace for water and composition in the regnerator. The biofuel species balance in the regenerator is omitted. Unit:kg/s

```
ifl             ref(feed_regenerator) && ref(drain_regenerator) then
mbwr:           drain_regenerator.mass * drain_regenerator.w_water = feed_regenerator.mass *
feed_regenerator.w_water + water_adsorbed;
mbcr:           drain_regenerator.mass * drain_regenerator.w_composition = feed_regenerator.mass *
feed_regenerator.w_composition;
endifl
```

## Energy balance

For simplicity reasons, both the adsorber and the regenerator are assumed to work isothermally.

```
eb:             feed_adsorber.t = drain_adsorber.t;
ifl             ref(feed_regenerator) && ref(drain_regenerator) then
ebr:            drain_regenerator.t = feed_regenerator.t;
endifl
```

## Pressure balance and compression work

The pressure drop of the adsorber can be defined. Unit: bar

```
pb:             drain_adsorber.p = feed_adsorber.p - delta_p_adsorber;
```

If the regenerator is connected, its pressure drop is defined. Unit: bar

```
ifl             ref(feed_regenerator) && ref(drain_regenerator) then
pbr:            drain_regenerator.p = feed_regenerator.p - delta_p_regenerator;
endifl
```

The compression work can be defined via the specific work

```
ifl             ref(pump_in) then
wc:             pump_in.power = feed_adsorber.mass * feed_adsorber.w_biofuel * spec_work;
endifl
```

## Test section

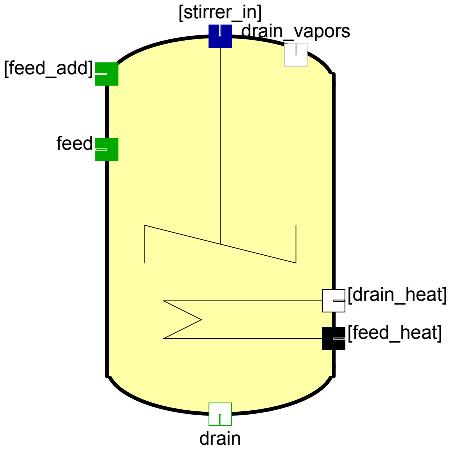
The correct connection and the correct biofuel setup is checked.

```
ifl             (ref(feed_regenerator) && !ref(drain_regenerator))|| (!ref(feed_regenerator) && ref
(drain_regenerator))
then
ts1:            test(0!=0)          error"feed_add or drain_add stream missing";
endifl
```

for both the adsorber and the regenerator, it is assumed that the composition of the biofuel does stays constant. This is a strong simplification, however, ethanol will typically be the only biofuel component, that will enter this unit.

```
ifl             (ref(feed_adsorber.Biofuel) && !ref(drain_adsorber.Biofuel)) || (!ref(feed_adsorber.Biofuel) &&
ref(drain_adsorber.Biofuel)) || ref (feed_adsorber.Biofuel) && ref (drain_adsorber.Biofuel) &&
(ref(feed_adsorber.Biofuel) != ref(drain_adsorber.Biofuel)))
then
tbiofuelad:     test (0!=0)         error "Use same biofuel object in feed and drain of the adsorber! ";
endifl
ifl             (ref(feed_regenerator.Biofuel) && !ref (drain_regenerator.Biofuel)) || (!ref(feed_regenerator.Biofuel)
&& ref(drain_regenerator.Biofuel)) || (ref(feed_regenerator.Biofuel) && ref (drain_regenerator.Biofuel) &&
(ref(feed_regenerator.Biofuel) != ref (drain_regenerator.Biofuel)))
then
tbiofuelreg:    test (0!=0)         error "Use same biofuel object in feed and drain of the regenerator! ";
endifl
```

## *BF_ETOH_FERMENTER - MODIFICATIONS*



### CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain |
| vapors: | drain_vapors |
| bio_stream: | feed_add (optional) |
| stream: | feed_heat (optional) |
| stream: | drain_heat (optional) |
| shaft: | stirrer_in (optional) |

### DESCRIPTION

An existing model form the APP_Bio_Lib was extendend. However, since the changes are significant the whole model is explained. The continous fermentation of monomeric sugars to ethanol, CO2 and yeast biomass. According to equations (6) and (7) both types of sugars (C5 and C6) can be converted. In addition yeast biomass formation according to equation (12) as well as byproduct formation according to equations (8) are (9) considered and the formatioThe nutrient demand is included via an elemntary balance. In the bio_streams that are fed to the fermentor and leave it, dry matter has to be specified as weender global object. There are two feed streams possible, as a result several cases have to be distinguished.

### VARIABLES

| | | |
|---|---|---|
| C5_to_biomass | Conversion of C5 sugars to yeast | [%] |
| C5_to_etoh | Conversion of C5 ethanol and CO2 | [%] |
| C5_moles_available | Moles of C5 Carbon available for microbbial metabolism | [kmol/s] |
| C6_to_biomass | Conversion of C6 sugars to yeast | [%] |
| C6_to_etoh | Conversion of C6ethanol and CO2 | [%] |
| C6_moles_available | Moles of C6 Carbon available for microbbial metabolism | [kmol/s] |
| stoich_O_demand | Stoichiometric demand of oxygen | [kg/s] |
| stoich_H_demand | Stoichiometric demand of hydrogen | [kg/s] |
| stoich_N_demand | Stoichiometric demand of nitogen | [kg/s] |
| N_input | Input of nitrogen via substrate | [kg/s] |
| initial_yeast_conc | Initial concentration of yeast | [g/l] |
| operating_t | Operating temperature | [°C] |
| operating_p | Operating pressure | [bar] |
| delta_p_htex | Pressure drop heat exchanger | [bar] |
| q_trans | Transferred heat | [kW] |
| spec_power_supply | Specific power input stirrer, power per volume | [kW/m³] |
| volume | Reaction volume | [m³] |
| time | Residence time in fermenter | [h] |

## EQUATIONS

Depending on wheter the feed_add is connected and wheter bioufel globals are referenced five cases can be distinguished. For simplicity reasons, in this documentation only case 1a is explained. In this case i) the feed_add connector is not used and ii) no bioufel global is referenced in the feed. The other cases (1b, 2a, 2b) can be explored by opening the library in IPSEpro's model development kit (MDK).

### Specific section for case 1a

No biofuel is referenced in the feed, however, since biofuel species are produced in the reactions, a biofuel global has to be specified in the drain.

```
ifl             !ref(feed_add) && (!ref(feed.Biofuel)&&ref(drain.Biofuel)) then
```

### The overall mass balance for case 1a

The stoichiometric demands of N, O and H have to be considered in the mass balance. Unit: kg/s

```
mbo1a:          feed.mass + stoich_N_demand +stoich_O_demand + stoich_H_demand  = drain.mass +
drain_vapors.mass;
```

The amount of C5 and C6 moles availabel is calculated. Only monomeric sugars can be used. Unit: kmol/s

```
mbc51a:         C5_moles_available = feed.mass * feed.w_drymatter * feed.Weender.CH_mono_C5 * 5 / 150;
mbc61a:         C6_moles_available = feed.mass * feed.w_drymatter * feed.Weender.CH_mono_C6 * 6 / 180;
```

### The mass balance for stream components

The drymatter balance is omitted.

Water is consumed in the formation of glycerol, a by-product of ethanol fermentation whose formantion is considered. 1% of sugars converted to ethanol are converted to glycerol.

```
mbw1a:          drain.mass * drain.w_water + drain_vapors.mass * drain_vapors.w_water + (C6_moles_available *
C6_to_etoh + C5_moles_available * C5_to_etoh ) * 0.01 * 1/3 * 18 = feed.mass * feed.w_water;
```

CO2 (composition) is formed at equimolar amounts to ethanol. 1/3 mol of CO2 is formed per mole of C consumed. 3% of sugars are converted to glycerol and acetic acid (see below).

```
mbco1a:         drain.mass * drain.w_composition + drain_vapors.mass * drain_vapors.w_composition = feed.mass
* feed.w_composition + (C6_moles_available* C6_to_etoh  + C5_moles_available * C5_to_etoh) * (1- 0.03) * 44 *
1/3;
```

The bioufel balance is omitted, since all biofuel species balances are included.

### The biofuel species balance

The ethanol balance. 3% of sugars are converted to acetic acid and glycerol, see below. Per mole of C in sugar, 1/3 mol of ethanol is formed. The molar mass of ethanol is 46 g/mol.

```
mbbfe1a:        drain.mass * drain.w_biofuel * drain.Biofuel.etoh + drain_vapors.mass * drain_vapors.w_biofuel
=feed.mass * feed.w_biofuel + (C6_moles_available* C6_to_etoh  + C5_moles_available * C5_to_etoh) * (1- 0.03)
* 46 *1/3;
```

The glycerol balance. 1% of sugars are converted to glycerol. Per mole of C in sugar, 1/3 mol of glycerol is formed. The molar mass of glycerol is92 g/mol.

```
mbbfg1a:        drain.mass * drain.w_biofuel * drain.Biofuel.glycerol = ( C6_moles_available * C6_to_etoh +
C5_moles_available * C5_to_etoh) * 0.01 * 92 *1/3;
```

The acetic acid balance. 2% of sugars are converted to acetic acid. Per mole of C in sugar, 1/2 mol of acetic acid is formed. The molar mass of acetic acid is60 g/mol.

```
mbbfh1a:        drain.mass * drain.w_biofuel * drain.Biofuel.acetic_acid = ( C6_moles_available * C6_to_etoh +
C5_moles_available  * C5_to_etoh) * 0.02 * 60 * 1/2;
```

The furfural balance. No furfural is in the feed (per definition in case 1a) and no furfural is formed.

```
mbbff1a:        drain.mass * drain.w_biofuel * drain.Biofuel.furfural = 0;
```

### The balance for weender species in the drymatter

Yeast biomass (CH_bact, P_bact_int, L_bact) is formed from the carbohydrates. The variable C_moles_available and the respective conversions are used. Unit: kg/s

Formation of cell mass. It is assumed that cell mass has a molar mas of 24.737 g/mol and the following composition: 40% Carbohydrate, 55% Protein, 5% Fat.

The formation of cell mass (CH_bact, P_bact_int, L_bact)…

```
w1a1a:          drain.mass * drain.w_drymatter * drain.Weender.CH_bact = feed.mass * feed.w_drymatter *
feed.Weender.CH_bact + 0.4 * 24.737 * (C5_moles_available * C5_to_biomass + C6_moles_available *
C6_to_biomass);
w1b1a:          drain.mass * drain.w_drymatter * drain.Weender.P_bact_int = feed.mass * feed.w_drymatter *
feed.Weender.P_bact_int + 0.55 * 24.737 * (C5_moles_available * C5_to_biomass + C6_moles_available *
C6_to_biomass);
w1c1a:          drain.mass * drain.w_drymatter * drain.Weender.L_bact = feed.mass * feed.w_drymatter *
feed.Weender.L_bact + 0.05 * 24.737 * (C5_moles_available * C5_to_biomass+ C6_moles_available *
C6_to_biomass);
```

The conversion of monmeric sugars. The balance for monomeric C6 sugars (CH_mono_C6) is omitted.

```
w41a:           drain.mass * drain.w_drymatter * drain.Weender.CH_mono_C5 = feed.mass * feed.w_drymatter *
feed.Weender.CH_mono_C5 * ( 1 - ( C5_to_biomass+ C5_to_etoh));
```

All other weender components pass the system uncoverted.

```
w21a:           drain.mass * drain.w_drymatter * drain.Weender.CH_starch = feed.mass * feed.w_drymatter *
feed.Weender.CH_starch;
w51a:           drain.mass * drain.w_drymatter * drain.Weender.CH_cell = feed.mass * feed.w_drymatter *
feed.Weender.CH_cell;
w61a:           drain.mass * drain.w_drymatter * drain.Weender.CH_hemicell = feed.mass * feed.w_drymatter *
feed.Weender.CH_hemicell;
w71a:           drain.mass * drain.w_drymatter * drain.Weender.CH_lignin = feed.mass * feed.w_drymatter *
feed.Weender.CH_lignin;
w81a:           drain.mass * drain.w_drymatter * drain.Weender.P_bact_ext = feed.mass * feed.w_drymatter *
feed.Weender.P_bact_ext;
w91a:           drain.mass * drain.w_drymatter * drain.Weender.P_plant = feed.mass * feed.w_drymatter *
feed.Weender.P_plant;
w101a:          drain.mass * drain.w_drymatter * drain.Weender.L_fats = feed.mass * feed.w_drymatter *
feed.Weender.L_fats;
 w111a:         drain.mass * drain.w_drymatter * drain.Weender.ash = feed.mass * feed.w_drymatter *
feed.Weender.ash;
```

### Energy balance, reaction volume and yeast concentration

The energy leaving the system via product streams (drain and vapors) equals to the heat that is fed to the system via incoming stream (feed) + the heat that is released through chemical reactions + the heat that is exchanged in the heat exchangers + heat induced via stirring. Heat of reaction is assumed to be 90 and 75 kJ/mol C6 and C5 sugar consumed, respectively (1/6 and 1/5 mole C6 and C5 sugar per mole Carbon). The enthalpy of vaporization of CO2 is included. Unit: kW

```
eb1a:           drain.mass * drain.h+ drain_vapors.mass * drain_vapors.h = feed.mass * feed.h +
C6_moles_available * ( C6_to_biomass + C6_to_etoh) * 90000 / 6 + C5_moles_available * ( C5_to_biomass +
C5_to_etoh) * 75000 / 5 + spec_power_supply * volume + (C6_moles_available* C6_to_etoh +
C5_moles_available * C5_to_etoh) * (1- 0.03) * 44 * 1/3 * 348.24 + q_trans;
```

The reaction or reactor volume is calculated based on the mass flow and the residence time. Unit: m³

```
vol1a:          volume = feed.mass * feed.v * time * 3600;
```

The calculation of the intial yest concentration. Unit: g/l

```
wyeast1a:       initial_yeast_conc = feed.mass * feed.w_drymatter * ( feed.Weender.P_bact_int +
feed.Weender.CH_bact + feed.Weender.L_bact) / feed.mass / feed.v;
```

Here the specfic section for case 1a ends. The cases 1b, 2a, 2b and 2c are not listed here (as indicated by the dots), but can be examined in the library using IPSEpro's MDK.

```
endifl
```

## Specific section for case 1b, 2a, 2b and 2c are not included

```
ifl             !ref(feed_add) && (ref(feed.Biofuel)&&ref(drain.Biofuel)) then
…
endifl
ifl             ref(feed_add) && (!ref(feed.Biofuel)&&ref(drain.Biofuel)) then
…
endifl
ifl             ref(feed_add) && (ref(feed.Biofuel)&&ref(drain.Biofuel)&&!ref(feed_add.Biofuel)) then
…
endifl
ifl             ref(feed_add) && (ref(feed.Biofuel)&&ref(drain.Biofuel)&&ref(feed_add.Biofuel)) then
…
endifl
```

## The general section

Here, the general section starts with the calculation of Nitrogen, Oxygen and Hydrogen demand. These quantities are used in the overall mass balance and are necessary for a correct elementary balance. Typically, the hydrogen and oxygen demand will be very close to 0, only a numerical uncertainty is remains. The nitrogen demand is unequal to zero and can be used to calculated the necessary amount of nutrients. Generally, the equations have the form: element demand = elemnt in product – element input. However, the nitrogen input is not considered because nitrogen may not be available for the microorganisms. Instead the Nitrogen input is calculated sepearately. Unit: kg/s

### Elementary balance

The calculation of the oxygen demand. Unit: kg/s

```
oxd1:           stoich_O_demand =
```

Oxgyen stored in biomass, the oxygen content in yeast is assumed to be 0.557 mol/mol C.

```
(C6_moles_available * C6_to_biomass + C5_moles_available * C5_to_biomass) * 0.557 * 16
```

- Oxygen liberated from sugars

```
 - ( C6_moles_available * C6_to_biomass + C5_moles_available * C5_to_biomass) *16
```

- Oxygen produced by glycerol production

```
 - ( C6_moles_available *  C6_to_etoh + C5_moles_available * C5_to_etoh ) * 0.01 * 1/3 * 16;
```

Similarly, the hydrogen deman is calculated as the hydrogen stored in biomass – hydrogen liberated from sugars. the oxygen content in yeast is assumed to be 1.613 mol/mol C.Unit: kg/s

```
hd1:            stoich_H_demand = (C6_moles_available *  C6_to_biomass + C5_moles_available *
C5_to_biomass) * 1.613 * 1 - ( C6_moles_available * C6_to_biomass + C5_moles_available * C5_to_biomass) * 2
*1;
```

For calculation of the nitrogen demand, no nitrogen input in the feed is considered in this equation. The nitrogen content in yeast is 0.158 mol/mol C. Unit: kg/s

```
nd1:            stoich_N_demand =  (C6_moles_available * C6_to_biomass + (C5_moles_available *
C5_to_biomass ) * 0.158 *14;
```

The nitrogen input is calculated depending on wheter feed_add is referenced or not. The nitrogen content of protein is 0.173 kg/kg Unit: kg/s

```
ifl             !ref(feed_add) then
nin1:           N_input = feed.mass* feed.w_drymatter*(feed.Weender.P_bact_int + feed.Weender.P_bact_ext
+feed.Weender.P_plant ) * 0.173;
elsel
nin2:           N_input = (feed.mass* feed.w_drymatter*(feed.Weender.P_bact_int + feed.Weender.P_bact_ext
+feed.Weender.P_plant)+(feed_add.mass*feed_add.w_drymatter*(feed_add.Weender.P_bact_int +
feed_add.Weender.P_bact_ext +feed_add.Weender.P_plant)))*0.173;
endifl
```

## Pressure balance, stirrer, heat exchangers

Assumption regarding the pressures and temperatures. Units: bar and °C

```
pb1:            drain.p = operating_p;
pb2:            drain_vapors.p = operating_p;
eb1:            drain.t = operating_t;
eb2:            drain_vapors.t = operating_t;
```

The power input via stirring. Only applies, if the stirrer is connected. Unit: kW

```
ifl             ref(stirrer_in) then
pw1:            stirrer_in.power = spec_power_supply * volume;
endifl
```

The mass, energy, and pressure balance for the heat exchanger.Only applies, if the heat exchanger is connected Units: kg/s, bar, kW

```
ifl             ref(drain_heat) && ref(feed_heat) then
mbh:            drain_heat.mass = feed_heat.mass;
ebht:           drain_heat.mass * drain_heat.h + q_trans = feed_heat.mass * feed_heat.h;
pb3:            drain_heat.p + delta_p_htex = feed_heat.p;
endifl
```

## The vapours liquid equilibrium

The distribution of all volatile compounds in the respective product streams (drain and drain_vapors). The solubility of CO2 in water in calculated using Henry's law. Unit: bar

```
mbcd:           drain.w_composition/ 44 / (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel / 46 ) *
fhenry_co2_water1(drain_vapors.t) = drain_vapors.p * drain_vapors.w_composition / 44 /
(drain_vapors.w_composition / 44 + drain_vapors.w_water / 18 + drain_vapors.w_biofuel / 46 );
```

The amount of water in the drain_vapors is calculated by using the acitivity coefficients for the binary system etahnol-water. Unit: bar

```
mbwv:           drain_vapors.p * drain_vapors.w_water / 18/ (drain_vapors.w_composition / 44 +
drain_vapors.w_water / 18 + drain_vapors.w_biofuel/ 46) = fptx_h2o(drain_vapors.t) * fgam_h2o (operating_t,
(drain.w_biofuel* drain.Biofuel.etoh/ 46)/ ( drain.w_biofuel* drain.Biofuel.etoh/ 46) + drain.w_water / 18) *
drain.w_water / 18 / (drain.w_composition / 44 + drain.w_water /  18 + drain.w_biofuel* drain.Biofuel.etoh/ 46);
```

Likewise, the amount of ethanol in the drain_vapors is calculated. Unit: bar

```
mbbfv:          drain_vapors.p * drain_vapors.w_biofuel/ 46 / (drain_vapors.w_composition / 44+
drain_vapors.w_water / 18+ drain_vapors.w_biofuel/ 46) = fptx_etoh(drain_vapors.t) * fgam_etoh
(operating_t,(drain.w_biofuel* drain.Biofuel.etoh/ 46)/ ( drain.w_biofuel* drain.Biofuel.etoh/ 46) + drain.w_water /
18) * drain.w_biofuel*drain.Biofuel.etoh / 46  / (drain.w_composition / 44 + drain.w_water / 18 + drain.w_biofuel*
drain.Biofuel.etoh/ 46);
```

## Test section

Test for negative pressure drops

```
tp1:            test(feed.p >= operating_p)    warning "feed pressure lower than operating_pressure";
ifl             ref(feed_add) then
tp2:            test(feed_add.p >= operating_p) warning "feed_add pressure lower than operating_pressure";
endifl
```

Test for weender setup

```
ifl         !ref(feed.Weender) || !ref(drain.Weender) then
tw1:        test(0!=0)          error "use weender global objects in feed and drain";
endifl
```

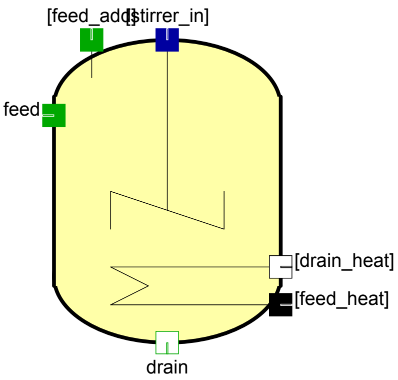
Test for biofuel setup

```
ifl         ref(feed.Biofuel)==ref(drain.Biofuel) then
tbfs2:      test(0!=0)          error"dont use same Biofuel global in feed and drain";
endifl
```

No conversions of sugars larger than 1

```
tc5:        test (C5_to_biomass + C5_to_etoh <= 1.0)        error "Sum of conversions of c5  sugars >= 1.0";
tc6:        test (C6_to_biomass + C6_to_etoh <= 1.0)        error "Sum of conversions of c6  sugars >= 1.0";
```

## *BF_ETOH_CELLULOSEDIGESTION – SUBMODEL OF BF_ETOH_PREPROCESSING – MODIFICATIONS*



### CONNECTORS

| | |
|---|---|
| shaft: | stirrer_in |
| bio_stream: | feed |
| bio_stream: | feed_add (optional) |
| bio_stream: | drain |
| stream: | feed_heat (optional) |
| stream: | drain_heat (optional) |

### DESCRIPTION

An existing model form the APP_Bio_Lib was extended. Since the changes are minor, only the new equations are shown here. The continous hydrolyses of cellulose (and hemicellulose) to monomeric sugars according to equations (1) and (2) (see section 2.3). The specific enzyme demand and the specific enzyme activity are used. In the bio_streams that are fed to the fermentor and leave it, dry matter has to be specified as weender global object. There are two feed streams possible, as a result several cases have to be distinguished. The new variables that were introduced, are shown in bold characters.

### VARIABLES

| | | |
|---|---|---|
| **spec_enzyme_supply** | **Specific enzyme supply FPU Enzyme per g cellulose** | **[FPU/g]** |
| **spec_activity** | **Specific activity of Enzyme** | **[FPU/g Enzyme]** |
| conv_cell | Conversion of cellulose to C6 monomers | [%] |
| conv_hemicell | Conversion of hemicellulose to C5 and C6 sugars | [%] |
| operating_p | Operating pressure | [bar] |
| operating_t | Operating temperature | [°C] |
| volume | Reactor volume | [m³] |
| **time** | **Residence time in the fermenter** | **[h]** |
| spec_power_supply | Specific power input stirrer | [kW/m³] |
| q_trans | Transferred heat | [kW] |
| **w_c5_hc** | **Weight fraction of C5 sugars in hemicellulose** | **[kg/kg]** |
| **wis_content** | **Water insoluble solid content at beginning** | **[kg/kg]** |
| delta_p_htex | Rressure drop heat exchanger | [bar] |

## NEW EQUATIONS

Since there are two feed streams, two cases have to be distinguished. Here, only case 1 is shown, in which the feed_add is not connected. The other case (2) can be explored by opening the library in IPSEpro's model development kit (MDK).

### Specific section for case 1

```
ifl                    !ref(feed_add) then
```

### Drymatter balance

The drymatter balance has to be modified, since the enzyme that is fed to the system is specified as part of the weender object. Previously there was only a supply variable. Unit: kg/s

```
mbdm1:                    drain.mass * drain.w_drymatter = feed.mass * feed.w_drymatter * ( 1 +
feed.Weender.CH_cell * conv_cell * (18/162) + feed.Weender.CH_hemicell * conv_hemicell * ( w_c5_hc * 18 / 132
+ ( 1 - w_c5_hc) * 18 / 162));
```

### Biofuel balance

The biofuel balance is omitted. Instead, the whole set of biofuel species balance is introduced. No formation of one of the biofuel species is assumed to take place. Unit:kg/s

```
bf11:                     drain.mass * drain.w_biofuel * drain.Biofuel.etoh = feed.mass * feed.w_biofuel *
feed.Biofuel.etoh;
bf21:                      drain.mass * drain.w_biofuel * drain.Biofuel.glycerol = feed.mass * feed.w_biofuel *
feed.Biofuel.glycerol;
bf31: drain.mass * drain.w_biofuel * drain.Biofuel.acetic_acid = feed.mass * feed.w_biofuel *
feed.Biofuel.acetic_acid;
bf41: drain.mass * drain.w_biofuel * drain.Biofuel.furfural = feed.mass * feed.w_biofuel * feed.Biofuel.furfural;
```

### Water insoluble solids, cellulase supply and reaction volume

The water insoluble solid fraction fed to reactor is calculated. It is assumed that hemicellulose, cellulose, lignin, starch, yeast and 50% of inorganics (ash) are insobule. Unit: kg/kg

```
wis1:                     wis_content =         feed.mass * feed.w_drymatter *  (feed.Weender.CH_hemicell +feed.
Weender.CH_cell + feed.Weender.CH_lignin  +feed. Weender.CH_starch + feed.Weender.CH_bact +
feed.Weender.P_bact_int + feed.Weender.L_bact + 0.5 *feed. Weender.ash ) / (feed.mass);
```

The amount of enzyme (defined by the weender species P_bact_ext), that is fed to the system is correlated with the specific enzyme supply and specific activity. Unit: kg/s

```
cb1:                      feed.mass * feed.w_drymatter * feed.Weender.P_bact_ext = spec_enzyme_supply /
spec_activity* feed.mass * feed.w_drymatter * feed.Weender.CH_cell;
```

The reaction volumne: Unit: $m^3$

```
vol1:              volume = feed.mass * feed.v  * time * 3600;
```

here the section for case 1 ends.

```
endifl
```

The general section is identical, however, there are some new tests in the test section

### Test section

The enzyme input must be larger than 0

```
ts2:               test(drain.Weender.P_bact_ext>0.0)     error "specify enzyme as P_bact_ext in one of the input
streams";
```

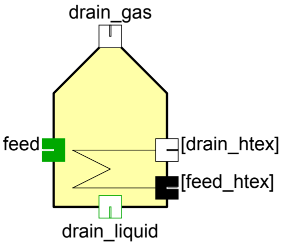
The conversions of cellulose and hemicellulose must be smaller than 0

```
t1:                test (conv_cell <= 1.0)                error "Cellulose conversion is greater than 1";
t2:                test ( conv_hemicell <= 1.0)           error "Hemicellulose conversion is greater than 1";
```

Biofuel setup. Presently biofuel globals have to be speficied.

```
ifl                !ref(feed.Biofuel) || !ref(drain.Biofuel)
then
tbfs1:             test (0!=0)                     error "Specify Biofuel in feed and drain by biofuel global!";
endifl
ifl                ref(feed_add)&&!ref(feed_add.Biofuel)
then
tbfs2:             test (0!=0)                     error "Specify Biofuel in feed_add by biofuel global!";
endifl
```

## *BF_EVAP – SUBMODEL OF BF_EVAP – MODIFICATIONS*



### CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain_liquid |
| stream: | drain_gas |
| stream: | feed_htex (optional) |
| stream: | drain_htex (optional) |

### DESCRIPTION

An existing model form the APP_Bio_Lib was extended. Since the changes are minor, only the new equations are shown here. This simple model can be used to simulate the evapoartion of a bio_stream (see section 2.3). The drymatter can be specified as elementary or weender. No chemical reactions are assumed to take place. The vapours are assumed to be pure water.

### VARIABLES

| | | |
|---|---|---|
| delta_p | Pressure drop feed stream | [bar] |
| q_trans | Transferred heat | [kW] |
| q_loss | Heat lost to the surrounding | [kW] |
| p | Pressure in the evaporator | [bar] |
| t | Temperature in the system | [°C] |
| x | Vapour fraction. Fraction of water that evaporates | [kg/kg] |
| dt | Temperature difference between the heating stream and the operating temperature | [°C] |
| area | Area necessary for heat transfer | [m²] |
| k | Heat transfer coefficient | [W/Km²] |
| bpe | Boiling point elevation | [°C] |
| delta_p_htex | Pressure drop heat exchanger | [bar] |

### EQUATIONS

#### General mass balances

The overall mass balance. Unit: kg/s

mbo: feed.mass = drain_liquid.mass + drain_gas.mass;

#### Mass balance of stream components

The water balance is omitted.

The biofuel balance. For simplicity reasons, it is assumed, that bioufel das not evaporate. Consequently, the same biofuel globals must be used in the drain and the feed. See test section. Unit: kg/s

mbbf: drain_liquid.mass * drain_liquid.w_biofuel = feed.mass * feed.w_biofuel;

The drymatter balance. All drymatter is recovered in the drain. Hence, the same weender globals must be used in the drain and the feed. See test section. Unit: kg/s

mbdm: drain_liquid.mass * drain_liquid.w_drymatter = feed.mass * feed.w_drymatter;

The composition balance. All compositiondrymatter is recovered in the drain. Unit: kg/s

mbc: drain_liquid.mass * drain_liquid.w_composition = feed.mass * feed.w_composition;

The calculation of the fraction of water, that evaporates. Unit: kg/kg

mbx: x = drain_gas.mass /(feed.mass*feed.w_water);

#### The energy balance and temperature assumptions

The general energy balance. Unit: kW

ebo: feed.mass * feed.h + q_trans = drain_liquid.mass * drain_liquid.h + drain_gas.mass * drain_gas.h + q_loss;

The calculation of the temperature in the liquid drain. The temperature is set 0.01°C below the saturation temperature at given p.Water is therefore in liquid state. Unit: °C

```
    eb3:            drain_liquid.t= ftpx(p, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)-0.01
```

The temperature in the vapors is assumed to be identical to the temperature in the evaporator. Unit: °C

```
    eb4:            t = drain_gas.t;
```

The correlation of temeparture and pressure in the system. The temperature in the system is assumed to be the saturation tempature of steam at the given pressure (x=1) plus the boilin point elevation. Unit: °C

```
    eb5:            t = ftpx(p, 1.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)+bpe;
```

## Pressure assumptions, boling point elevation, calculation of heat exchanger area

Pressure assumption. Unit: bar

```
    pb0:            p = feed.p - delta_p;
    pb1:            drain_gas.p= p;
    pb2:            drain_gas.p = drain_liquid.p;
```

The calculation of the boiling point elevation, that is calculated in an external function (fbpe). Unit: °C

```
    bpe1:           bpe=fbpe(drain_liquid.w_drymatter)
```

## Heat exchanger

```
    ifl             (ref(drain_htex) && ref(feed_htex)) then
```

The mass balance. Unit: kg/s

```
    mbh:            drain_htex.mass = feed_htex.mass;
```

The energy balance. Unit: kW

```
    ebht:           drain_htex.mass * drain_htex.h + q_trans = feed_htex.mass * feed_htex.h;
```

The pressure assumptions. Unit: bar

```
    pb3a:           drain_htex.p + delta_p_htex = feed_htex.p;
```

The definition of the temperature difference. The temperature in heat exchanger is calucated as the arithmethic mean of feed and drain temepature. If the heat exchanger is not connected, dt must be set. Unit: °C

```
    dt1:            dt=(feed_htex.t+drain_htex.t)/2 - t;
```

The calculation of the area necessary for heat exchange. Unit: kW

```
    dt2:            1000*q_trans=area*dt*k;
    endifl
```

## Test section

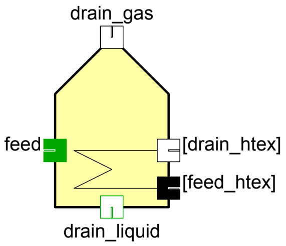
The setup of the globals. The same weender, elementary and biofuel globals have to be used in the feed and the drain.

```
    ifl             ref(feed.Weender) != ref(drain_liquid.Weender) then
    ts1:            test(0!=0)          error "use same weender global object for feed and drain_liquid";
    endifl
    ifl             ref(feed.Elementary) != ref(drain_liquid.Elementary) then
    ts1:            test(0!=0)          error "use same elementary global object for feed and drain_liquid";
    endifl
    ifl      (ref(feed.Biofuel) && !ref (drain_liquid.Biofuel)) || (!ref(feed.Biofuel) && ref (drain_liquid.Biofuel)) ||
    (ref(feed.Biofuel) && ref (drain_liquid.Biofuel) && (ref(feed.Biofuel) != ref (drain_liquid.Biofuel)))  then
    tbiofuel01:     test (0!=0)                 error "Use same biofuel object in feed and drain_liquid! ";
    endifl
```

Check for 2nd law thermodynamics in the heat exchanger.

```
    ifl             ref(drain_htex) && ref(feed_htex) then
    tdt1:           test(dt>0) warning "Heating stream is colder than solution to be evaporated";
    endifl
```

## *BF_FLASH – SUBMODEL OF BF_EVAP – NEW UNIT*



## CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain_liquid |
| stream: | drain_gas |
| stream: | feed_htex (forbidden!) |
| stream: | drain_htex (forbidden!) |

## DESCRIPTION

A simple model for a flash unit. The drymatter can be specified as elementary or weender. No chemical reactions are assumed to take place. In contrast to the evaporation unit, this unit work adiabatically, i.e. no heat exchange takes place. Consequently, the existing heat exchanger connectors must not be connected. Neither is the bpe included.

## VARIABLES

| | | |
|---|---|---|
| delta_p | Pressure drop | [bar] |
| p | Pressure in the system | [bar] |
| t | Temperature in the system | [°C] |
| x | Vapour fraction. Fraction of water that evaporates | [kg/kg] |

## EQUATIONS

### General mass balances

The overall mass balance and the calculation of x. Units: kg/s and kg/kg

```
f1:          feed.mass = drain_liquid.mass + drain_gas.mass;
mbx:         x = drain_gas.mass /(feed.mass*feed.w_water);
```

### Stream components mass balance

The water balance is omitted.

The biofuel balance. Biofuel is assumed not to evaporate. Unit: kg/s

```
mbbf:        drain_liquid.mass * drain_liquid.w_biofuel = feed.mass * feed.w_biofuel;
```

The drymatter and the composition balance. These species are assumed not to evaporate either. Unit: kg/s

```
mbdm:        drain_liquid.mass * drain_liquid.w_drymatter = feed.mass * feed.w_drymatter;
mbc:         drain_liquid.mass * drain_liquid.w_composition = feed.mass * feed.w_composition;
```

### Energy balance & temperature assumptions

The overall energy balance. No heat exchange with surrounding. Unit: kW

```
e1:          feed.mass * feed.h = drain_liquid.mass * drain_liquid.h + drain_gas.mass * drain_gas.h;
```

The enthalpy of the gas is assumed to be that of saturated steam at the respective pressure.

```
eb1:         drain_gas.h = fhpx(p,1.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

The calculation of the temperature in the liquid drain. The temperature is set 0.01°C below the saturation temperature at given p.Water is therefore in liquid state. Unit: °C

```
eb3:         drain_liquid.t= ftpx(p, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)-0.01;
```

The temperature in the vapors is assumed to be identical to the temperature in the evaporator. Unit: °C

```
eb4:         t = drain_gas.t;
```

### Pressure assumptions

```
pb1:         feed.p = p + delta_p;
pb2:         drain_liquid.p = p;
pb3:         drain_gas.p = p;
```

### Test section

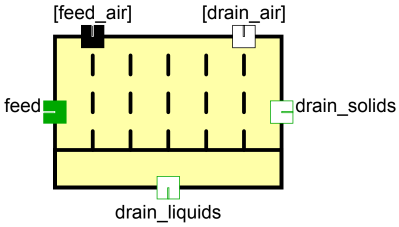
A check for the correct global setup

```
ifl          ref(feed.Weender) != ref(drain_liquid.Weender) then
ts1:         test(0!=0)          error "use same weender global object for feed and drain_liquid";
endifl
ifl          ref(feed.Elementary) != ref(drain_liquid.Elementary) then
ts2:         test(0!=0)          error "use same elementary global object for feed and drain_liquid";
endifl
ifl     (ref(feed.Biofuel) && !ref (drain_liquid.Biofuel)) || (!ref(feed.Biofuel) && ref (drain_liquid.Biofuel)) ||
(ref(feed.Biofuel) && ref (drain_liquid.Biofuel) && (ref(feed.Biofuel) != ref (drain_liquid.Biofuel)))  then
ts3:         test (0!=0)         error "Use same biofuel object in feed and drain_liquid!";
endifl
```

The connection of a heat exchanger is forbidden

```
ifl          ref(drain_htex) || ref (feed_htex) then
ts4:         test(0!=0)  error "disconnect the heat exchanger. No balances for heat exchanger included";
endifl
```

## *BF_FILTERPRESS – NEW UNIT*



### CONNECTORS

bio_stream: feed
bio_stream: drain_liquids
bio_stream: drain_solids
stream: feed_air (optional)
stream: drain_air (optional)

### DESCRIPTION

A model for the separation of solids and liquids. The liquid fraction also contains soluble solids. Insobule solids are recovered in the solid fraction, however, only to a certain degree (retention). The drymatter has to be specified as weender global. Solubles, composition and biofuel have the same concetrations in all the streams (with respect to water!) The solubility of ash can be chosen. The model resembles the filterpress, described in section 2.3.9.1). Therefore, pressurized air is used to operate it.

### VARIABLES

| | | |
|---|---|---|
| solubilty_ash | Mass fraction of ash that is soluble | [kg/kg] |
| retention_insolubles | Mass fraction of insolubles that passes the filter | [kg/kg] |
| c_factor | Concentration factor. Defined as the ratio water in solids | [kg/kg] |
| delta_p_solids | Pressure drop of solid fraction | [bar] |
| delta_p_liquids | Pressure drop of liquid fraction | [bar] |
| delta_p_air | Pressured drop of air | [bar] |
| spec_air_supply | Amount of pressurized air per kg feed | [kg/kg] |
| dt | Temperature drop | [°C] |
| q_loss | Heat that is lost to the surroundings | [kW] |

### EQUATIONS

#### The general mass balance

The overall mass balance for the filterpress. Unit: kg/s

mb: feed.mass = drain_liquids.mass + drain_solids.mass;

#### The mass balance of stream components

The water balance is omitted. The composition, the biofuel and the drymatter are conserved (no chemical reactions). Unit: kg/s.

mc: feed.mass * feed.w_composition = drain_liquids.mass* drain_liquids.w_composition + drain_solids.mass * drain_solids.w_composition;
mbf: feed.mass * feed.w_biofuel = drain_liquids.mass* drain_liquids.w_biofuel + drain_solids.mass * drain_solids.w_biofuel;
mbdm: feed.mass * feed.w_drymatter = drain_liquids.mass * drain_liquids.w_drymatter + drain_solids.mass* drain_solids.w_drymatter;

#### The mass balance of the weender species

The lignin balance is omitted. Generally, no conversion of weender species takes place. Unit: kg/s

mw1: feed.mass * feed.w_drymatter * feed.Weender.CH_bact = drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_bact + drain_liquids.mass * drain_liquids.w_drymatter * drain_liquids.Weender.CH_bact;
mw2: feed.mass * feed.w_drymatter * feed.Weender.CH_starch = drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_starch + drain_liquids.mass * drain_liquids.w_drymatter * drain_liquids.Weender.CH_starch;

```
mw3:            feed.mass * feed.w_drymatter * feed.Weender.CH_mono_C5 = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.CH_mono_C5 + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.CH_mono_C5;
mw4:            feed.mass * feed.w_drymatter * feed.Weender.CH_mono_C6 = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.CH_mono_C6 + drain_liquids.mass * drain_liquids.w_drymatter
*drain_liquids.Weender.CH_mono_C6;
mw5:            feed.mass * feed.w_drymatter * feed.Weender.CH_cell = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.CH_cell + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.CH_cell;
mw6:            feed.mass * feed.w_drymatter * feed.Weender.CH_hemicell= drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.CH_hemicell + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.CH_hemicell;
mw8:            feed.mass * feed.w_drymatter * feed.Weender.P_bact_ext = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.P_bact_ext + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.P_bact_ext;
mw9:            feed.mass * feed.w_drymatter * feed.Weender.P_bact_int = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.P_bact_int + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.P_bact_int;
mw10:           feed.mass * feed.w_drymatter * feed.Weender.P_plant = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.P_plant + drain_liquids.mass * drain_liquids.w_drymatter
*drain_liquids.Weender.P_plant;
mw11:           feed.mass * feed.w_drymatter * feed.Weender.L_bact = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.L_bact + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.L_bact;
mw12:           feed.mass * feed.w_drymatter * feed.Weender.L_fats = drain_solids.mass *
drain_solids.w_drymatter * drain_solids.Weender.L_fats + drain_liquids.mass * drain_liquids.w_drymatter *
drain_liquids.Weender.L_fats;
mw13:           feed.mass * feed.w_drymatter * feed.Weender.ash = drain_solids.mass * drain_solids.w_drymatter *
drain_solids.Weender.ash + drain_liquids.mass * drain_liquids.w_drymatter * drain_liquids.Weender.ash;
```

The retention of componets is modelled using the concentration factor (c_factor). This factor is defined as the ratio of mass flow of water in the solids and in the feed. Unit: kg/s

```
water:          c_factor * feed.mass * feed.w_water = drain_solids.mass * drain_solids.w_water;
```

The composition and biofuel stream componets behaves identically to water. Unit: kg/s

```
rc:             drain_solids.mass*drain_solids.w_composition = feed.mass*feed.w_composition * c_factor;
rbf:            drain_solids.mass*drain_solids.w_biofuel =  feed.mass* feed.w_biofuel * c_factor;
```

## The distribution of insoubles and solubles in the drain_liquids and drain_solids stream

The retention of water insolubles (yeast, starch, cellulose, hemicellulose, lignin and the insoluble part of ash). Through the mass balance it is ensured, that Unit: kg/s

```
rw1:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_bact = feed.mass *
feed.w_drymatter * feed.Weender.CH_bact * retention_insolubles;
rw9:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.P_bact_int = feed.mass
*feed.w_drymatter * feed.Weender.P_bact_int * retention_insolubles;
rw11:           drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.L_bact = feed.mass
*feed.w_drymatter * feed.Weender.L_bact * retention_insolubles;
rw2:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_starch = feed.mass
*feed.w_drymatter * feed.Weender.CH_starch *retention_insolubles;
rw5:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_cell = feed.mass *
feed.w_drymatter * feed.Weender.CH_cell * retention_insolubles;
rw6:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_hemicell = feed.mass *
feed.w_drymatter * feed.Weender.CH_hemicell * retention_insolubles;
rw7:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_lignin =feed.mass *
feed.w_drymatter * feed.Weender.CH_lignin * retention_insolubles;
rw13:           drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.ash = feed.mass
*feed.w_drymatter * feed.Weender.ash * (1-solubilty_ash) * retention_insolubles + feed.mass *feed.w_drymatter *
feed.Weender.ash * solubilty_ash * c_factor;
```

Solubles (monmeric sugars, enzymes, plant protein, extractives) behave like water. To model this behaviour the concentration factor is applied. Unit: kg/s.

```
rw3:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_mono_C5 = feed.mass *
feed.w_drymatter * feed.Weender.CH_mono_C5 * c_factor;
rw4:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.CH_mono_C6 = feed.mass *
feed.w_drymatter * feed.Weender.CH_mono_C6 * c_factor;
rw8:            drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.P_bact_ext = feed.mass *
feed.w_drymatter * feed.Weender.P_bact_ext * c_factor;
```

```
rw10:           drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.P_plant = feed.mass *
feed.w_drymatter * feed.Weender.P_plant * c_factor;
rw12:           drain_solids.mass * drain_solids.w_drymatter * drain_solids.Weender.L_fats = feed.mass *
feed.w_drymatter * feed.Weender.L_fats * c_factor;
```

## Energy balance and temperature assumptions

A temperature drop can be considered. The temperature of drain_solids and drain_liquids is assumed to be indetical. Unit: °C

```
t1:             feed.t = drain_solids.t + dt;
t2:             feed.t = drain_liquids.t + dt;
```

Energy is conserved, however, a loss to the surrounding can be considered. Unit: kW

```
eb0:            feed.mass * feed.h = drain_liquids.mass * drain_liquids.h + drain_solids.mass * drain_solids.h +
q_loss;
```

## Air supply

```
ifl             ref(feed_air) && ref(drain_air) then
asmb1:          feed_air.mass = feed.mass * spec_air_supply;
asmb2:          feed_air.mass = drain_air.mass;
asp:            feed_air.p = drain_air.p + delta_p_air;
ash:            feed_air.h = drain_air.h;
endifl
```

## The test section

The setup of the biofuel globals

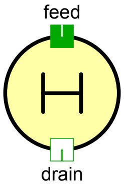
```
Ifl     ref(feed.Biofuel)&&(!ref(drain_solids.Biofuel) || !ref(drain_liquids.Biofuel)) then
        tbs1:   test(0!=0)                                  error "use biofuel globals in drain streams";
endifl


ifl ref(feed.Biofuel)!=ref(drain_solids.Biofuel) || ref(feed.Biofuel)!=ref(drain_liquids.Biofuel)  then
        tbs2:   test(0!=0)                                  error "use same biofuel globals in feed and drain streams";
endifl
```

Drymatter must be specified as Weender globals

```
ifl (!ref(feed.Weender) || (!ref(drain_liquids.Weender) || (!ref(drain_solids.Weender)))) then
        tw1:    test(0!=0)                                           error "use weender globals to specify drymatter";
endifl
```

## *BF_HEATSOURCE – NEW UNIT*



### CONNECTORS

bio_stream: feed
bio_stream: drain

### DESCRIPTION

A simple unit that can be used to heat or cool a biostream. Using this unit, no heat exchange with another stream is necessary.

### VARIABLES

| | | |
|---|---|---|
| q_trans | Heat transferred | [kW] |
| delta_t | Temeperature difference between feed and drain stream | [°C] |

### EQUATIONS

The mass balance. The mass is conserved. Unit: kg/s

```
f1:             feed.mass=drain.mass;
```

Energy balance. q_trans is positive when the ingoing stream is heated and negative when it is cooled. Unit: kW

```
f2:             feed.mass*feed.h+q_trans=drain.mass*drain.h;
```

The pressure balance. No pressure drop is considered. Unit: bar

```
f3:            feed.p=drain.p;
```

The temperature difference is defined. It is positive when the ingoing stream is heated. Unit: °C

```
f4:            feed.t+delta_t=drain.t;
```

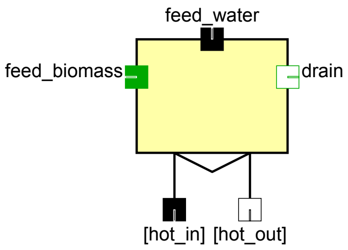
Species mass balance. Unit: kg/kg

```
mcb:           feed.w_biofuel      = drain.w_biofuel;
mcdm:          feed.w_drymatter    = drain.w_drymatter;
mcc:           feed.w_composition= drain.w_composition;
```

Thje test section. Check for correct setup of globals.

```
ifl            (ref(feed.Weender)&&!ref(drain.Weender)) || (!ref(feed.Weender) && ref(drain.Weender)) ||
(ref(feed.Weender) && ref  (drain.Weender) && (ref(feed.Weender) != ref (drain.Weender)))
then
tWeender01:    test (0!=0)                    error "Use same Weender object in feed and drain! ";
endifl
ifl            (ref(feed.Elementary)&&!ref(drain.Elementary)) || (!ref(feed.Elementary) && ref(drain.Elementary)) ||
(ref(feed.Elementary) && ref (drain.Elementary) && (ref(feed.Elementary) != ref(drain.Elementary)))
then
tElementary01:test (0!=0)                     error "Use same Elementary object in feed and drain! ";
endifl
ifl            (ref(feed.Biofuel)&&!ref(drain.Biofuel)) || (!ref(feed.Biofuel) && ref(drain.Biofuel)) || (ref(feed.Biofuel)
&&ref (drain.Biofuel) && (ref(feed.Biofuel) !=ref (drain.Biofuel)))
then
tBiofuel01:    test (0!=0)                    error "Use same biofuel object in feed and drain! ";
endifl
```

## *BF_LIQUID_HOT_WATER – NEW UNIT- THIS UNIT IS NOT USED IN THIS WORK BUT IN OTHER PROJECTS*



### CONNECTORS

bio_stream: feed_biomass
bio_stream: drain
stream: feed_water
stream: hot_in (optional)
stream: hot_out (optional)

### DESCRIPTION

A simple unit model for the liquid hot water pretreatment of biomass . it is assumed that water remains in the liquid state (i.e. the operation pressure in the unit is higher than the saturation pressure of water at the respective temperature). In the present version of this model, no chemical reactions take place.

### VARIABLES

| | | |
|---|---|---|
| p_operation | Operation pressure | [bar] |
| delta_p | Pressured drop | [bar] |
| t_operation | Operation temperature | [°C] |
| x_hot_out | The steam quality x in the heat exchanger drain | [kg/kg] |
| q_trans | Heat transferred by heat-exchanger | [kW] |
| delta_p_HEX | Pressure drop in the heat exchanger | [bar] |

## EQUATIONS

### Mass balances

The overall mass balance. Unit: kg/s

```
mb1:        feed_biomass.mass + feed_water.mass = drain.mass;
```

The species balance. The composition balance is omitted.

The mass balance for water., biofuel and drymatter. Unit: kg/s

```
mbw:        feed_biomass.w_water * feed_biomass.mass + feed_water.mass = drain.w_water * drain.mass;
mbb:        feed_biomass.w_biofuel * feed_biomass.mass = drain.w_biofuel * drain.mass;
mbdm:       feed_biomass.w_drymatter * feed_biomass.mass = drain.w_drymatter * drain.mass;
```

### Energy balances

The overall energy balance. q_trans is defined as the difference between energy in the drain and energy in the feed. Unit: kW

```
e1:         feed_biomass.mass * feed_biomass.h + feed_water.mass * feed_water.h + q_trans = drain.mass *
drain.h;
```

The tempearutre in the drain is equal to the operating temperature. Unit: kW

```
e2:         drain.t = t_operation;
```

All water remains ins liquid state. The operation temperature is 0.01°C smaller than the condensation temperature at the exit of the unit (p_operation – delta_p).

```
e3:         t_operation + 0.01 = ftpx(p_operation - delta_p, 0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

### Pressure assumptions

The pressure in the biomass feed is identical the operation pressure. Likewise the pressure in the feed_water has to be set to the same value. (see test section) Unit: bar

```
p1:         feed_biomass.p = p_operation;
```

The pressure drop in the unit is defined. Unit: bar

```
p2:         p_operation - delta_p = drain.p;
```

### Heat exchanger

When the heat exchanger is connected, the following equations apply:

```
ifl         ref (hot_in) && ref (hot_out) then
```

Mass balance of the heat exchanger. Unit: kg/s

```
hx1:        hot_in.mass = hot_out.mass;
```

Energy balance of the heat exchanger. Unit: kW

```
hx2:        hot_in.mass * hot_in.h = q_trans + hot_out.mass * hot_out.h;
```

The steam quality in the exit of the heat exchanger is calculated. Unit: kJ/kg

```
hx3:        hot_out.h = fhpx(hot_out.p, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) * (1-x_hot_out) + fhpx(hot_out.p,
1.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) * x_hot_out;
```

Pressured drop of the heat exchanger. Unit: bar

```
hx4:        hot_in.p - hot_out.p = delta_p_HEX;
```

Test for the heat exchanger

```
test_HEX1:  test(hot_out.h>0)     error "energy content of HEX water stream too little";
test_HEX2:  test(hot_in.t > t_operation) error "t_in too low";
test_HEX3:  test(hot_out.t > t_operation) error "t_in is still too low";
elsel
```

If the heat exchanger is not connected, x_hot_out is set to 0.

```
hx3a:       x_hot_out =0.0;
endifl
```

### Test section

The pressure in the feed_water has to be set to the same value as the pressure in the feed_biomass.

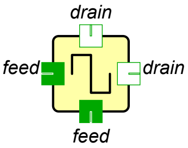
```
test1:      test(feed_biomass.p-feed_water.p==0)  error "Pressures of feed & water have to be the same!";
```

Test to check for the setup of global ojects (Weender, Elementary, Biofuel)

```
ifl         (ref(feed_biomass.Weender)&&!ref(drain.Weender)) || (!ref(feed_biomass.Weender) &&
ref(drain.Weender)) || (ref (feed_biomass.Weender) && ref(drain.Weender) && (ref(feed_biomass.Weender) !=ref
(drain.Weender)))
then
tWeender01: test (0!=0)                 error "Use same Weender object in feed_biomass and drain! ";
endifl
ifl         (ref(feed_biomass.Elementary)&&!ref(drain.Elementary)) || (!ref(feed_biomass.Elementary) &&
ref(drain.Elementary)) || ref (feed_biomass.Elementary) && ref (drain.Elementary) &&
(ref(feed_biomass.Elementary) != ref(drain.Elementary)))
then
tElementary01:test (0!=0)               error "Use same Elementary object in feed_biomass_biomass and
drain! ";
endifl
```

```
ifl             (ref(feed_biomass.Biofuel)&&!ref(drain.Biofuel)) || (!ref(feed_biomass.Biofuel) && ref(drain.Biofuel))
|| (ref(feed_biomass.Biofuel) && ref (drain.Biofuel) && (ref(feed_biomass.Biofuel) != ref (drain.Biofuel)))
then
tBiofuel01:     test (0!=0)                 error "Use same biofuel object in feed_biomass_biomass and drain! ";
endifl
```

## *BF_COD_BIOFUEL – SUBMODEL OF BF_MONITOR_BIOSTREAM – NEW UNIT*



### CONNECTORS

bio_stream: feed
bio_stream: drain

### DESCRIPTION

A monitor unit that calculates the chemical oxygen demand (COD) of the biofuel components in a bio_stream. Three different forms (massflow, massfraction and concentration) of the COD are calculated. For a definition of the COD see section 2.3. Due to the structure of the biostream, the drymatter must be defined by a global object (Weender or Elementary), even if the content of drymatter is 0. In the calculation of the COD, the drymatter is not considered.

### VARIABLES

| | | |
|---|---|---|
| COD_mass | COD massflow in the stream | [kg/s] |
| COD_massfrac | COD concentration in the stream | [g/kg] |
| COD_conc | Concentration of COD | [mg/l] |

### EQUATIONS

#### Conservation of mass, composition, temperature and pressure

The stream passes the monitor unchanged. Hence, the massflow does not change. Unit: kg/s

```
xfm:            drain.mass = feed.mass;
```

The stream passes the monitor unchanged. Hence, the composition does not change. Unit: kg/s

```
xfbf:           drain.w_biofuel = feed.w_biofuel;
xfdm:           feed.w_drymatter = drain.w_drymatter;
xfc:            drain.w_composition = feed.w_composition;
```

The stream passes the monitor unchanged. Hence, the temperatuere and pressure do not change. Units: °C and bar

```
xft:            drain.t = feed.t;
xfp:            drain.p = feed.p;
```

#### The calculation of the chemical oxygen demand

Depending on wheter a biofuel global is referenced in the stream or not, the COD is calculated

```
Ifl             !ref(feed.Biofuel) then
```

If no biofuel global is referenced, biofuel is defined as ethanol. Per g of Ethanol 2.09 g of oxygen are necessary for complete oxidation to CO2 and H2O. Unit: kg/s

```
cod1a:          COD_mass = feed.mass * feed.w_biofuel * 2.09;
```

if a biofuel global is referenced in the stream, the total COD of the stream is calculated as the sum the COD of the respective biofuel components. Unit: kg/s

```
elsel
```

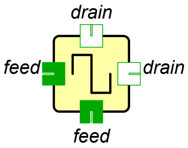
Per g of glycerol, acetic acid and furfural 1.22 g, 1.07 g and 1.67 g of oxygen are necessary for complete oxidation to CO2 and H2O. Unit: kg/s

```
cod1b:          COD_mass = feed.mass * feed.w_biofuel * (feed.Biofuel.etoh *2.09 + feed.Biofuel.glycerol *1.22 +
feed.Biofuel.acetic_acid* 1.07+feed.Biofuel.furfural*1.67);
endifl
```

Based on the massflow of COD the massfraction of COD and the concentration are calculated. Units: g/kg and g/l

```
cod2b:          COD_massfrac = COD_mass * 1000 / (feed.mass);
cod3b:          COD_conc= COD_mass * 1000 * 1000 / (feed.mass*feed.v*1000);
```

## *BF_COD_ELEMENTARY SUBMODEL OF BF_MONITOR_BIOSTREAM – NEW UNIT*



### CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain |

### DESCRIPTION

A monitor unit that calculates the chemical oxygen demand (COD) of all organic matter in a bio_stream. Three different forms (massflow, massfraction and concentration) of the COD are calculated. For a definition of the COD see section ref!. The organic matter must be specified by an elementary global. In addition, the massflow and concentration of volatile solids (organic drymatter) is calculated.

### VARIABLES

| | | |
|---|---|---|
| n | Stoichiometric coefficient for C acc. to the definition of the COD | [kmol/s] |
| a | Stoichiometric coefficient for H acc. to the definition of the COD | [kmol/s] |
| b | Stoichiometric coefficient for O acc. to the definition of the COD | [kmol/s] |
| c | Stoichiometric coefficient for N acc. to the definition of the COD | [kmol/s] |
| COD_mass | COD massflow in the stream | [kg/s] |
| COD_massfrac | Mass fraction of COD (per kg drymatter) | [kg/kg] |
| COD_conc | Concentration of COD | [g/l] |
| VS_mass | Massflow of volatile solids | [kg/s] |
| VS_conc | Concentration of volatile solids | [g/l] |

### EQUATIONS

#### Conservation of mass, composition, temperature and pressure

The stream passes the monitor unchanged. Hence, the massflow does not change. Unit: kg/s

xfm: drain.mass = feed.mass;

The stream passes the monitor unchanged. Hence, the composition does not change. Unit: kg/s

xfbf: drain.w_biofuel = feed.w_biofuel;
xfdm: feed.w_drymatter = drain.w_drymatter;
xfc: drain.w_composition = feed.w_composition;

The stream passes the monitor unchanged. Hence, the temperatuere and pressure do not change. Units: °C and bar

xft: drain.t = feed.t;
xfp: drain.p = feed.p;

#### Calculation of the stoichiometric constants

The stoichiometric constants for C, H, O and N according to the definition of the COD are calculated. Unit: kmol/s

fn: n= feed.mass * feed.w_drymatter * feed.Elementary.myC / 12.011;
fa: a= feed.mass * feed.w_drymatter * feed.Elementary.myH / 1.00794;
fb: b= feed.mass * feed.w_drymatter * feed.Elementary.myO / 15.9994;
fc: c= feed.mass * feed.w_drymatter * feed.Elementary.myN / 14.0067;

#### Calculation of COD and VS

The COD of the bio_stream (mass, massfraction and concentration) is calculated according to its definition. Units: kg/s, kg/kg and g/l

fcod: COD_mass = (n + a/4 - b/2 -3/4*c) * 15.9994*2;
fcod1: COD_massfrac= COD_mass/(feed.mass * feed.w_drymatter);
fcod2: COD_conc= COD_mass / (feed.mass * feed.v);

The massflow and concentration of volatile solids is calculated. Units: kg/s and g/l

fvs1: VS_mass = feed.mass * feed.w_drymatter * (1 -feed.Elementary.myAsh);
fvs2: VS_conc = VS_mass / (feed.mass  * feed.v);

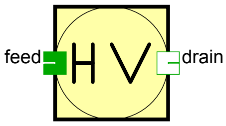
#### Test section

The correct setup of globals is tested

ifl ref(feed.Weender) then

ts1: test(0!=0) error "Don't use Weender global. For calculation of the COD of a bio_stream with Weender global, convert Weender to Elementary";
endifl
ifl !ref(feed.Elementary) then
ts2: test(0!=0) error "Use Elementary global to define biomass ";
endifl

## *BF_MONITOR_HV – NEW UNIT*



### CONNECTORS

bio_stream: feed
bio_stream: drain

### DESCRIPTION

A model that calculates the heating value of a biostream and the associated energy flow of the stream. There are various models included for the calculation of the heating value.

### VARIABLES & SWITCH

| | | |
|---|---|---|
| LHV_total | Lower heating value of the stream at standard conditions | [kJ/kg] |
| LHV_dry | Lower heating value of the drymatter in the stream at standard conditions | [kJ/kg] |
| HHV_dry | Higher heating value of the stream at standard conditions water and ash free | [kJ/kg] |
| ef_LHV_total | Energy flow of stream based on LHV_total | [kW] |
| ef_HHV_dry | Energy flow of stream based on HHV_dry | [kW] |
| ef_LHV_dry | Energy flow of stream based on LHV_dry | [kW] |
| myC | Mass fraction C in the stream | [kg/kg] |
| myH | Mass fraction H in the stream | [kg/kg] |
| myN | Mass fraction N in the stream | [kg/kg] |
| myO | Mass fraction O in the stream | [kg/kg] |
| myS | Mass fraction S in the stream | [kg/kg] |
| myCl | Mass fraction Cl in the stream | [kg/kg] |
| myAsh | Mass fraction Ash in the stream | [kg/kg] |
| HV_Source (Boie, OLS, PLS, user_defined, Verbandsformel) | Allows the user to choose the source for calculating the heating value of biomass (switch) | |

### EQUATIONS

Depending on the global setup in the biostream, five cases can be distinguished. For simplicity reasons here only case 1 is shown, in which the drymatter in the biostream is defined by an elementary global.

#### Mass balance

General mass balance and stream component mass balance The total massflow and the components mass fraction is conserved. The composition balance is omitted. Units: kg/s and kg/kg

mb1: feed.mass = drain.mass;
mb2: feed.w_water = drain.w_water;
mb3: feed.w_biofuel = drain.w_biofuel;
mb4: feed.w_drymatter = drain.w_drymatter;

#### Temperature and pressure

The temperature and pressure are conserved. Units: bar and °C

p1: feed.p = drain.p;
t1: feed.t = drain.t;

#### Case specific section

Case 1, When elementary is connected, the variables speficying the biomass composition are identical to the element mass fraction in the feed. Unit: kg/kg

ifl (ref(feed.Elementary) && ref(drain.Elementary)) then
e11: myC = feed.Elementary.myC;
e12: myH = feed.Elementary.myH;
e13: myN = feed.Elementary.myN;

```
e14:                    myO = feed.Elementary.myO;
e15:                    myS = feed.Elementary.myS;
e16:                    myCl = feed.Elementary.myCl;
e17:                    myAsh = feed.Elementary.myAsh;
endifl
```

For cases 2 trough 5, the elementary mass fraction is calculated from the weender and biofuel globals. For abbreviation, these equations are not shown here but can be inspected using IPSEpro'S model development kit.

```
ifl
…
endifl
ifl
…
endifl
ifl
…
endifl
ifl
…
endifl
```

### Calulation of the heating value

Via a switch the user can choose different models for the calculation of the heating or set the heating value (user defined).
The OLS model [Friedl *et al.* , 2005] is a model for the higher heating value of dry biomass. Unit: kJ/kg

```
ifl             HV_Source == OLS then
                fhhv_oLs :          HHV_dry = 1.87 * (myC*100)^2 - 144 * myC *100 - 2820 * myH * 100 + 63.8 *
(myC *100 * myH*100) + 129 * myN*100 + 20147;
endifl
```

Likewhis the PLS model [Friedl *et al.* , 2005] is a model for the higher heating value of dry biomass. Unit: kJ/kg

```
ifl             HV_Source == PLS then
                fhhv_pls:  HHV_dry = 5.22 * (myC*100)^2 - 319 * myC * 100 - 1647 * myH *100 + 38.6 * (myC *100
* myH * 100) + 133 * myN *100 + 21028;
endifl
```

The Boie formula [Kaltschmitt *et al.* , 2009] calculates the Lower heating value of water and ash free biomass. Unit: kJ/kg

```
ifl             HV_Source == Boie then
                fheat_value_Boie2: LHV_dry = (34835 * myC + 93870 * myH+ 10465 * myS+ 6280 * myN - 10800 *
myO) * (1- feed.w_drymatter * myAsh);
endifl
```

The „Verbandsformel" [Stephan *et al.* , 2010] is a model for the calculation of the lower heating value of moist biomass. Unit: kJ/kg

```
ifl             HV_Source == Verbandsformel then
                fheat_value_VF1:   LHV_total= ((33.900 * myC + 121.40 * myH + 10.500 * myS-15.200 * myO) * (
        feed.w_drymatter +feed.w_biofuel) - feed.w_water * 2.44)*1000;
endifl
```

When the option "user defined" is chosen, the user can set one of the heating values. Unit: kJ/kg

```
ifl             HV_Source == user_defined then
endifl
```

### Calculation of energy flows

Based on the heating values, the energy flows of the stream are calculated. Unit: kW

```
eg1:            ef_LHV_total = feed.mass * LHV_total;
eg2:            ef_LHV_dry = feed.mass * (feed.w_drymatter + feed.w_biofuel) * LHV_dry;
eg3:            ef_HHV_dry = feed.mass  * (feed.w_drymatter + feed.w_biofuel) * HHV_dry;
```

### Conversion of the heating values

Depending on the model, one type of heating value is obtained. Using the equations below, the other types are calculated.
To obtain the higher heating value of the drymass the enthalpy of vaporization has to be added to the lower heating of the drymass. Water formed through oxidation of H has to be considered. Unit: kJ/kg

```
fhv1:           LHV_dry  = HHV_dry            - 18.0125/(2 *1.00794) *  myH * 2442.6;
```

To obtain the lower heating value of a moist stream, reference base has to be changed and the enthaply of vaporization of water in the feed has to be substracted.

```
fhv2:           LHV_total = LHV_dry * (1 - feed.w_water- feed.w_composition) - feed.w_water *2442.6;
```

### Test section

The correct setup of globals is checked.

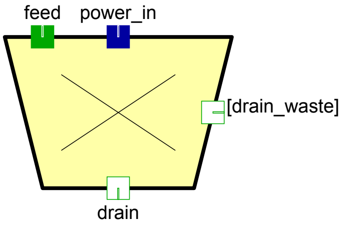
```
ifl             ref(feed.Weender)&&!ref(drain.Weender) || !ref(feed.Weender)&&ref(drain.Weender) || (ref
(feed.Weender) && ref(drain.Weender)) && ref(feed.Weender) != ref(drain.Weender) then
ts1:            test(0!=0) error "Connect same Weender to feed and drain!";
```

```
endifl

ifl         ref(feed.Elementary)&&!ref(drain.Elementary) || !ref(feed.Elementary)&&ref(drain.Elementary) || (ref
(feed.Elementary) && ref(drain.Elementary)) && ref(feed.Elementary) != ref(drain.Elementary) then
ts2:        test(0!=0) error "Connect same Elementary to feed and drain!";
endifl

ifl         ref(feed.Biofuel)&&!ref(drain.Biofuel) || !ref(feed.Biofuel)&&ref(drain.Biofuel) || (ref(feed.Biofuel) &&
ref(drain.Biofuel)) && ref(feed.Biofuel) != ref(drain.Biofuel) then
t3:         test(0!=0) error "Connect same Biofuel to feed and drain!";
endifl
```

### *BF_SIZE_REDUCTION – NEW UNIT*



## CONNECTORS

| | |
|---|---|
| bio_stream: | feed |
| bio_stream: | drain |
| shaft: | power_in |
| bio_stream: | drain_waste (optional) |

## DESCRIPTION

A simple unit for the size reduction of biomass. Part of the biomass can separated from the drain, if desired (e.g. bark).

## VARIABLES

| | | |
|---|---|---|
| spec_energy_consumption | Energy necessary to reduce size of biomass | [kJ/kg] |
| waste_fraction | Fraction of biomass, that is not used in the process (e.g. bark) | [kg/kg] |

## EQUATIONS

Depending on whether the drain_waste is connected, two cases have to be distinguished.

```
ifl         ref(drain_waste) then
```

### **Case 1 drain_waste is connected**

### Mass balance

The overall mass balance. Unit: kg/s

```
mo:         feed.mass =drain.mass + drain_waste.mass;
```

The definition of the waste fraction. Unit: kg/s

```
mbw:        drain_waste.mass = feed.mass * waste_fraction;
```

The mass balance of stream components. The water balance is omitted. Unit: kg/s

```
mcb:        feed.mass * feed.w_biofuel = drain.mass * drain.w_biofuel + drain_waste.mass *
drain_waste.w_biofuel;
mcdm:       feed.mass * feed.w_drymatter = drain.mass * drain.w_drymatter + drain_waste.mass
*drain_waste.w_drymatter;
mcc:        feed.mass * feed.w_composition = drain.mass * drain.w_composition +  drain_waste.mass *
drain_waste.w_composition;
```

The comopisition of the drain and the drain_waste are indetical. Unit: kg/kg

```
mcb1:       drain.w_biofuel = drain_waste.w_biofuel;
mcdm1:      drain.w_drymatter = drain_waste.w_drymatter;
mcc1:       drain.w_composition = drain_waste.w_composition;
```

### Pressure and temperature assumptions

For simplicity reasons, the pressure and temperature of the feed and the drain waste are identical. Units: bar and °C

```
p2:         feed.p = drain_waste.p;
t2:         feed.t = drain_waste.t;
```

### Case 2 drain_waste is not connected

For the case that no drain_waste is connected, the following equations apply.

```
      elsel
```

#### Mass balance

Overall mass balance and waste fraction. Units: kg/s and kg/kg

```
      mo1:            feed.mass =drain.mass;
      mbw1:           waste_fraction = 0;
```

The mass balance of stream components. The water balance is omitted. Unit: kg/s

```
      mcb2:           feed.w_biofuel =  drain.w_biofuel;
      mcdm2:          feed.w_drymatter = drain.w_drymatter;
      mcc2:           feed.w_composition = drain.w_composition;
      endifl
```

### General section

#### Pressure and temperature assumptions

For simplicity reasons, the pressure and temperature of the feed and the drain are identical. Units: bar and °C

```
      p1:             feed.p = drain.p;
      t1:             feed.t = drain.t;
```

#### Energy consumption

The specific energy consumption is defined. Unit: kW

```
      e1:             power_in.power =   feed.mass * spec_energy_consumption;
```

### Test section

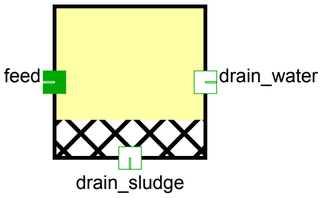
Biomass must be defined by a Weender object.

```
      ifl             ref(feed.Biofuel) || ref(drain.Biofuel) || ref (drain_waste.Biofuel)
      then
      tbiofuel1:      test (0!=0) error "Dont use Biofuel gloabl in this unit ";
      endifl
      ifl             ref(feed.Elementary) || ref(drain.Elementary) || ref (drain_waste.Elementary)
      then
      tElementary1:  test (0!=0) error "Dont use Elementary gloabl in this unit ";
      endifl
```

The correct setup of the Weender globals is checked.

```
      ifl             (ref(feed.Weender)&&!ref(drain.Weender) || (!ref(feed.Weender) && ref(drain.Weender)) || (ref
      (feed.Weender) && ref (drain.Weender) && (ref(feed.Weender) != ref (drain.Weender)))
      then
      tweender01:               test (0!=0)                     error "Use same weender object in feed and drain!";
      endifl
```

## *BF_SLUDGE_SEPARATOR – NEW UNIT*



### CONNECTORS

```
      bio_stream:               feed
      bio_stream:               drain_water
      bio_stream:               drain_sludge
```

### DESCRIPTION

A separator model that separates a biostream with an elementary object in the feed into two biostreams. It was developed to balance the formation of sludge in aerobic treatment or anaerobic digestion but can be used for other purposes as well.

## VARIABLES

| | | |
|---|---|---|
| dp_water | Pressure drop o water | [bar] |
| dp_sludge | Pressure drop of sludge | [bar] |
| sludge_formed | Amount of sludge formed | [kg/s] |
| sludge_moisture | Moisture content of sludge | [kg/kg] |
| ash_recovery | Mass fraction of ash that is recovered in sludge | [kg/kg] |
| N_recovery | Fraction of N input that is recovered in Sludge | [kg/kg] |
| S_recovery | Fraction of S input that is recovered in Sludge | [kg/kg] |
| Cl_recovery | Fraction of Cl input that is recovered in Sludge | [kg/kg] |
| C_recovery | Fraction of C input that is recovered in Sludge | [kg/kg] |
| O_recovery | Fraction of O input that is recovered in Sludge | [kg/kg] |
| H_recovery | Fraction of H input that is recovered in Sludge | [kg/kg] |

## EQUATIONS

### Mass balances

The overall mass balance. Unit: kg/s

mb1: feed.mass = drain_sludge.mass + drain_water.mass;

The stream compoents balance. The water balance is omitted. Unit: kg/s

dm1: feed.mass * feed.w_drymatter = drain_sludge.mass * drain_sludge.w_drymatter + drain_water.mass* drain_water.w_drymatter;

bf1: feed.mass * feed.w_biofuel = drain_water.mass * drain_water.w_biofuel + drain_sludge.mass * drain_sludge.w_biofuel;

c1: feed.mass * feed.w_composition = drain_water.mass * drain_water.w_composition + drain_sludge.mass * drain_sludge.w_composition;

The elementary balance. Ash is omitted. Unit: kg/s

ebC: feed.mass * feed.w_drymatter * feed.Elementary.myC = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myC+ drain_water.mass * drain_water.w_drymatter * drain_water.Elementary.myC;

ebH: feed.mass * feed.w_drymatter * feed.Elementary.myH = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myH + drain_water.mass * drain_water.w_drymatter * drain_water.Elementary.myH;

ebO: feed.mass * feed.w_drymatter * feed.Elementary.myO = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myO + drain_water.mass* drain_water.w_drymatter * drain_water.Elementary.myO;

ebN: feed.mass * feed.w_drymatter * feed.Elementary.myN = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myN + drain_water.mass * drain_water.w_drymatter * drain_water.Elementary.myN;

ebS: feed.mass * feed.w_drymatter * feed.Elementary.myS = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myS + drain_water.mass * drain_water.w_drymatter * drain_water.Elementary.myS;

ebCl: feed.mass * feed.w_drymatter * feed.Elementary.myCl = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myCl + drain_water.mass * drain_water.w_drymatter * drain_water.Elementary.myCl;

The recoveries for the elements in the sludge. Unit: kg/s

rC: C_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myC) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myC;

rH: H_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myH) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myH;

rO: O_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myO) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myO;

rAsh: ash_recovery *(feed.mass * feed.w_drymatter * feed.Elementary.myAsh) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myAsh;

rN: N_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myN) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myN;

rS: S_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myS)= drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myS;

rCl: Cl_recovery * (feed.mass * feed.w_drymatter * feed.Elementary.myCl) = drain_sludge.mass * drain_sludge.w_drymatter * drain_sludge.Elementary.myCl;

The formation of sludge and its moisture. Units: kg/s and kg/kg

s1: sludge_formed = drain_sludge.mass * drain_sludge.w_drymatter;

sm1: sludge_moisture = drain_sludge.w_water;

### Temperature, pressure, cp and v assumptions

The temperature is conserved across the unit. Unit: °C

```
tb1:            feed.t= drain_water.t;
tb2:            feed.t = drain_sludge.t;
```

The pressure drop of drain_water and drain_sludge are defined. Unit: bar

```
pb1:            drain_water.p = feed.p - dp_water;
pb2:            drain_sludge.p = feed.p - dp_sludge;
```

For simplicity reasons and due to the lack of data, the heat capacity and the specific volume of the drymatter is identical in the feed and the drains. Units: kJ/kg°C and $m^3/kg$

```
fcp1:           drain_water.Elementary.cp = feed.Elementary.cp;
fcp2:           drain_sludge.Elementary.cp = feed.Elementary.cp;
fv1:            drain_water.Elementary.v = feed.Elementary.v;
fv2:            drain_sludge.Elementary.v = feed.Elementary.v;
```

## Test section

Only biostream that reference elementary globals can be connected to the unit.

```
ifl             ref(feed.Weender) || ref(drain_water.Weender) || ref(drain_sludge.Weender) then
tweender:       test (0!=0) error "Dont use Weender global in this unit ";
endifl
ifl             ref(feed.Biofuel) || ref(drain_water.Biofuel) || ref (drain_sludge.Biofuel) then
tBiofuel:       test (0!=0) error "Dont use Biofuel global in this unit ";
endifl
```

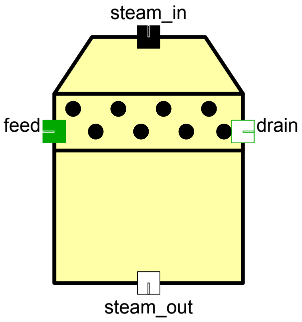
The drymatter has to be specified by elementary globals.

```
ifl             !ref(feed.Elementary) || !ref(drain_water.Elementary) || !ref(drain_sludge.Elementary) then
telementary1:   test (0!=0) error "Specify drymatter by Elementary globals" ;
endifl
```

Different globals must be used in the feed and the drains.

```
ifl             ref(feed.Elementary)==ref(drain_sludge.Elementary) || ref(feed.Elementary) ==
ref(drain_water.Elementary) || ref(drain_water.Elementary) ==ref(drain_sludge.Elementary) then
telementary2:   test (0!=0) error "Dont use same Elementary globals in the feed and drain!";
endifl
```

## *BF_STEAM_DRYER – NEW UNIT*



### CONNECTORS

stream:            steam_in
stream:            steam_out
bio_stream:        feed
bio_stream:        drain

### DESCRIPTION

A model for a dryer that uses steam as a drying medium. Superheated steam is used to dry solids in direct contact. As aproducts, dried solids and saturated secondary steam are obtained.

### VARIABLES

| | |
|---|---|
| p | Operating pressure in the dryer [bar] |
| delta_p_solids_release | Pressure drop when solids are released [bar] |
| delta_p_solids_feed | Pressure differenece between solids feed and operating pressure [bar] |
| delta_p_steam_in | Pressure drop of steam [bar] |
| dt_in | Temperature difference between biomass stream and heating steam [°C] |
| q_trans | Transferred heat from heating steam to biomass [kW] |

| | |
|---|---|
| q_loss | Heat lost to the surrounding [kW] |

# EQUATIONS

## Mass balances

The overall mass balance. Unit: kg/s

```
bmb1:        feed.mass + steam_in.mass = drain.mass + steam_out.mass;
```

The components mass balance. The water balance is omitted. Unit: kg/s

```
dmb1:        feed.mass* feed.w_drymatter = drain.mass* drain.w_drymatter;
```

For simplicity reasons, no biofuel and no composition is assumed to prevail in the vapors. Unit: kg/s

```
bfb1:        feed.mass* feed.w_biofuel = drain.mass* drain.w_biofuel;
cb1:         feed.mass*feed.w_composition = drain.mass * drain.w_composition;
```

No weender or elematary mass balances are needed because the composition of drymatter is assumed to be constant.

## Energy balances

The overall energy balance. Unit: kW

```
ebo:         feed.mass * feed.h + steam_in.mass * steam_in.h = drain.mass * drain.h + steam_out.mass*
steam_out.h + q_loss;
```

The product steam is assumed to be saturated at the operationg temperature. Unit: kJ/kg

```
eb1:         steam_out.h = fhpx(p,1.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

The biomass leaves the system 0.01°C below the condensation temperature of steam at the given pressure, i.e. water is in the liquid state. Unit: °C

```
eb2:         drain.t= ftpx(drain.p, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)-0.01;
```

The temperature difference between at the inlet, i.e. between heating steam and biomass to be dried. Unit: °C

```
eb3:         dt_in = steam_in.t - feed.t;
```

The heat transfer from steam to biomass. Unit: kW

```
eb4:         q_trans = steam_in.mass* (steam_in.h -steam_out.h);
```

## Pressure balances

The pressure drops of solids at the inlet and at solids release are defined. Unit: bar

```
pb0:         p - delta_p_solids_feed= feed.p;
pb1:         p - delta_p_solids_release = drain.p;
```

The pressure of the secondary steam is identical to the operating pressure in the system. Unit: bar

```
pb2:         steam_out.p= p;
```

The pressure drop of the steam entering the system. Unit: bar

```
pb3:         steam_in.p - delta_p_steam_in = p;
```

## Test section

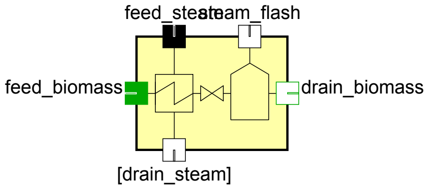
Check for correct setup of the globals.

```
ifl          ref(feed.Weender) != ref(drain.Weender) then
ts1:         test(0!=0) error"Use same weender global object for feed and drain_liquid";
endifl
ifl          ref(feed.Elementary) != ref(drain.Elementary) then
ts2:         test(0!=0) error"Use same Elementary global object for feed and drain_liquid";
endifl
ifl          (ref(feed.Biofuel)&&!ref(drain.Biofuel)) || (!ref(feed.Biofuel) && ref(drain.Biofuel)) || (ref (feed.Biofuel)
&& ref (drain.Biofuel) && (ref(feed.Biofuel) != ref (drain.Biofuel))) then
tbiofuel01:          test (0!=0)               error "Use same biofuel object in feed and drain_liquid! ";
endifl
```

Test for 2$^{nd}$ law thermodynamics.

```
ts3:         test(steam_in.h>steam_out.h) error"steam_in.h is smaller steam_out.h!";
```

## *BF_STEAM_EXPLOSION SUBMODEL BF_STEAM_EXPLOSION_DSI_WEENDER – MODIFICATIONS*



## CONNECTORS

| | |
|---|---|
| stream: | feed_steam |
| stream: | drain_steam (not used in this submodel) |
| bio_stream: | feed_biomass |
| bio_stream: | drain_biomass |
| stream: | steam_flash |

## DESCRIPTION

A model for the steam explosion of biomass. In this model it is assumed that Direct steam injection (DSI) is applied to heat up the biomass to the necessary conditions. After a certain residence time, the biomass is flashed to obtain secondary steam and the slurry. The conversion of cellulose and hemicellulose to sugars and by-products according to equations (xyz) is considered. In addition, the conversion of acetyl groups to acetic acid is considered. The input of sufluric acid (or $SO_2$) and neutralizing agent is considered using demand variables. An existing unit was modified to inclued chemical reactions.

## VARIABLES & SWITCH

| | | |
|---|---|---|
| t_operation | Operation temperature of the unit | [°C] |
| p_operation | Operation pressure of the unit | [bar] |
| delta_p_valve | Pressure drop of the release valve | [bar] |
| p_release | Release pressure after the steam explosion | [bar] |
| E | Void volume fraction of total volume | [-] |
| holdup_time | Hold up time of the biomass in the unit | [s] |
| q_trans | Heat transfered from steam to biomass in the unit | [kW] |
| q_loss | Heat loss to the surroundings | [kW] |
| mass_cond | Massflow of steam that condensates in the unit | [kg/s] |
| V_total | Total volume of the unit | [m³] |
| spec_q_in | Specific energy input into the unit | [kJ/kgDM] |
| hemicell_sugar | Conversion of hemicellulose to sugars | [kg/kg] |
| hemicell_degraded | Conversion of hemicellulose to byproducts | [kg/kg] |
| cell_sugar | Conversion of cellulose to sugars | [kg/kg] |
| cell_degraded | Conversion of icellulose to byproducts | [kg/kg] |
| w_c5_hc | Mass fraction of C5-Polymer in hemicellulose | [kg/kg] |
| w_acetic_acid_hc | Mass fraction of acetyl groups in hemicellulose | [kg/kg] |
| acid_in | Mass flow of acid in | [kg/s] |
| spec_acid | Specific demand of Sulfuric acid per kg water in biomass | [kg/kg] |
| ammonia_in | Demand of ammonia to neutralize sulfuric acid | [kg/s] |
| Calculate_Ammonia_Demand (No, Yes) (switch) | Calculates the demand of Ammonia necessary for neutralization | |

## EQUATIONS

### Mass balances

### The overall mass balance.

The input of $SO_2$ and ammonia that is modeled using demand variables and end up in the ash fraction of the drymatter has to be considered. The conversion to $H_2SO_4$ and ammonium is considered. Unit: kg/s

```
fm1:        feed_biomass.mass+ feed_steam.mass+ acid_in * 96/64 + ammonia_in * 18/17 =
drain_biomass.mass + steam_flash.mass;
```

### The stream components mass balance

The water balance is omitted. Units: kg/s
No CO2 is formed.

```
fm5:        feed_biomass.w_composition * feed_biomass.mass = drain_biomass.w_composition *
drain_biomass.mass;
```

The drymatter balance. Here, all chemical reactions that change the amount of dry matter (e.g. hydrolyis of a polymeric sugar to monomers), has to be considered. The amount drymatter leaving the system is identical to the amount entering (1) + the amount formed in chemical reactions – the amount converted to non-dry matter components (e.g. formation of acetic acid from acetyl grouops). Drymatter is formed in the hydrolysis of C5 polymer in hemicellulose, where one molecule of water is added per mole of C5 polymer in hemicellulose.

```
fm4:        feed_biomass.w_drymatter * feed_biomass.mass * (1 + feed_biomass.Weender.CH_hemicell *
hemicell_sugar * ( w_c5_hc * ( 18/ 132 )
```

Drymatter is also formed in the hydrolysis of C6 polymer in hemicellulose…

```
+ (1 - w_c5_hc - w_acetic_acid_hc) * ( 18/ 162))
```

and in the hydrolysis of cellulose.

```
+ feed_biomass.Weender.CH_cell * cell_sugar * 18 / 162
```

Finally, drymatter is added via $SO_2$ and $NH_3$. In the drain, these inorganics are balanced as part of the ash.

```
+ acid_in*96/64 + ammonia_in*18/17
```

Drymatter is converted to biofuel by reaction of acetyl groups to acetic acid…

```
- feed_biomass.Weender.CH_hemicell *w_acetic_acid_hc
```

and in the degradation reactions of hemicellulose (to biofuel)…

```
- feed_biomass.Weender.CH_hemicell *(1-w_acetic_acid_hc) * hemicell_degraded
```

and cellulose.

```
- feed_biomass.Weender.CH_cell * cell_degraded) = drain_biomass.w_drymatter*drain_biomass.mass;
```

## The biofuel species balance

The formation of the biofuel components furufal and acetic acid is considered.

Biofuel globals in the feed are not allowed. Hence, biofuel in the feed is ethanol. Since no ethanol is formed, ethanol mass is conserved. Unit: kg/s

```
fsbf1:          feed_biomass.mass * feed_biomass.w_biofuel = drain_biomass.mass * drain_biomass.w_biofuel *
drain_biomass.Biofuel.etoh;
```

No glycerol is allowed in the feed, and no glycerol is formed. Unit: kg/s

```
fsbf2:          0 = drain_biomass.mass * drain_biomass.w_biofuel * drain_biomass.Biofuel.glycerol;
```

Acetic acid is formed from hemicellulose. Unit: kg/s

```
fsbf3:          feed_biomass.w_drymatter * feed_biomass.mass * feed_biomass.Weender.CH_hemicell *
w_acetic_acid_hc = drain_biomass.mass * drain_biomass.w_biofuel * drain_biomass.Biofuel.acetic_acid;
```

Furfural is formed as degradation product from hemicellulose and cellulose. Unit: kg/s

```
fsbf4:          feed_biomass.w_drymatter * feed_biomass.mass * (feed_biomass.Weender.CH_hemicell *
hemicell_degraded* ( w_c5_hc * 96/132 + (1-w_c5_hc-w_acetic_acid_hc ) * 126/ 162)          # furfural formed in
reaction 5) + feed_biomass.Weender.CH_cell * cell_degraded * 126/ 162) = drain_biomass.mass *
drain_biomass.w_biofuel * drain_biomass.Biofuel.furfural;
```

## The weender species balance

Here, the conversion of the biomass is modeled. Polymeric sugars are hydrolysed to monomers or degraded, all other biomass components do not react. $SO_2$ and ammonia are converted to $H_2SO_4$ and ammonium and end up in the ash. Unit: kg/s

```
fsb1:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_bact =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.CH_bact;
fsb2:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_starch =
drain_biomass.mass * drain_biomass.w_drymatter *drain_biomass.Weender.CH_starch;
fsb3:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_mono_C5 +
feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_hemicell * w_c5_hc * (150 / 132 ) *
hemicell_sugar = drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.CH_mono_C5;
fsb4:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_mono_C6 +
feed_biomass.mass * feed_biomass.w_drymatter * ( feed_biomass.Weender.CH_hemicell * (1- w_c5_hc-
w_acetic_acid_hc) * ( 180/ 162) * hemicell_sugar + feed_biomass.Weender.CH_cell * cell_sugar * ( 180/ 162)) =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.CH_mono_C6;
fsb5:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_cell * ( 1-
cell_sugar-cell_degraded) = drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.CH_cell;
fsb6:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.CH_lignin =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.CH_lignin;
fsb7:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.P_bact_ext =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.P_bact_ext;
fsb7a:          feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.P_bact_int =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.P_bact_int;
fsb8:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.P_plant =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.P_plant;
fsb9:           feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.L_bact =
drain_biomass.mass * drain_biomass.w_drymatter *drain_biomass.Weender.L_bact;
fsb10:          feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.L_fats =
drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.L_fats;
fsb11:          feed_biomass.mass * feed_biomass.w_drymatter * feed_biomass.Weender.ash + ammonia_in *
(18/17)  + acid_in * (96/64) = drain_biomass.mass * drain_biomass.w_drymatter * drain_biomass.Weender.ash;
```

## Acid input and neutralisation by ammonia

If desired (switch), the ammonia demand necessary for neutralization can be calculated.

```
Ifl             Calculate_Ammonia_Demand == Yes then
```

The calculation of the ammonia demand. The neutralization capacity of ash (0.0025), is considered. Unit: kg/s

```
fac:            ammonia_in = 17 * ( acid_in/ 64 + drain_biomass.mass*drain_biomass.w_biofuel*
drain_biomass.Biofuel.acetic_acid / 60 - feed_biomass.mass * feed_biomass.w_drymatter
*feed_biomass.Weender.ash *0.0025 );
elsel
```

```
    fac2:               ammonia_in =0;
    endifl
```

The acid input and the specific acid demand (in % of dry biomass fed to the system) are considered. Unit: kg/s

```
    fac1:               acid_in = spec_acid * feed_biomass.mass * feed_biomass.w_drymatter;
```

## The energy balances

The overall energy balance. Unit: kW

```
    f8:                 feed_biomass.mass*feed_biomass.h + feed_steam.mass*feed_steam.h =
    steam_flash.mass*steam_flash.h + drain_biomass.mass*drain_biomass.h + q_loss;
```

The specific energy input is defined. Unit: kJ/kg

```
    fe1:                spec_q_in = q_trans/(feed_biomass.mass*feed_biomass.w_drymatter);
```

The definition of the heat that is transferred from steam to biomass is defined. Unit: kW

```
    fe1a:               q_trans = q_loss + feed_biomass.mass * (fhpx(p_operation, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,
    0)*feed_biomass.w_water + feed_biomass.fht_biomass (t_operation)* feed_biomass.w_drymatter -
    feed_biomass.h);
```

The heat that is transferred from steam to biomass correlates with the amount of steam that is condensed. Unit: kW

```
    fe2:                q_trans  = mass_cond * ( feed_steam.h - fhpx(p_operation, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0))
    + (feed_steam.mass - mass_cond) * ( feed_steam.h - fhpx(p_operation, 1, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0));
```

The void fraction and the amount of steam that is not condesed are correlated. Unit: kg/s

```
    fm2:                feed_steam.mass - mass_cond = (E * V_total/holdup_time - mass_cond *
    fv(p_operation,fhpx(p_operation, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0),1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)) /
    fv(p_operation,fhpx(p_operation, 1.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0),1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

## Volume and operating conditions

The total volume is correlated with void fraction, residence time and holup time. Unit: $m^3$

```
    f1:                 V_total=feed_biomass.mass*holdup_time*feed_biomass.v*(1+E/(1-E));
```

The operating temperature is assumed to be saturation temperature at the operating pressure. Unit: °C

```
    f2:                 t_operation=ftpx(p_operation, 0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

## Pressure assumptions and conditions of streams leaving the system (flash steam and biomass)

The pressure drop of the valve and the release pressure are correlated with the operating pressure. Unit: bar

```
    fp2:                p_operation-delta_p_valve=p_release;
```

The release pressure of the unit is identical to the pressure of product streams (flash steam and biomass) Unit: bar

```
    f4:                 p_release  = steam_flash.p;
    f5:                 p_release  = drain_biomass.p;
```

The flashed steam is saturated (x=1). Unit: kJ/kg

```
    f6:                 steam_flash.h = fhpx(p_release, 1.0 ,1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0);
```

The temperature of the biomass product is 0.01°C below the saturation temperature at the respective pressure. Unit: °C

```
    f7:                 drain_biomass.t = ftpx(p_release, 0.0, 1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0)-0.01;
```

## Test section

The pressure of the steam must be higher than that of in the unit.

```
    t1:   test (p_operation < feed_steam.p) warning "steam p < operation p";
```

The pressure in the unit must be higher than that of the product streams.

```
    t2:                 test (delta_p_valve>=0.0)      warning "delta_p < 0.0";
```

The drain_steam connector must not be used.

```
    ifl                 ref(drain_steam) then
    ts:                 test (0!=0) error "Dont connect drain steam with this submoldel!";
    endifl
```

The toal volume must be larger than the volume of biomass and condensate.

```
    t3a:  test ((((feed_biomass.mass*feed_biomass.w_water + mass_cond)*fv(p_operation,fhpx(p_operation, 0.0, 1.0,
    0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0),1.0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) +feed_biomass.mass *
    feed_biomass.w_drymatter * feed_biomass.Weender.v) * holdup_time) < V_total) warning "V total < Volume
    Biomass + Condensate";
```

Test of correct global setup. Biofuel is formed through chemical reactions in the unit.Therefore, a biofuel global must be referenced in the drain.

```
    ifl                 !ref(drain_biomass.Biofuel) then
    tbs1:               test (0!=0) error "Use Biofuel global in drain_biomass";
    endifl
```

However, in the feed no biofuel is allowed.

```
    ifl                 ref(feed_biomass.Biofuel) then
    tbs2:               test (0!=0) error "Dont Use Biofuel global in feed_biomass";
    endifl
```

No elementary globals are allowed in the unit.

```
    ifl                 ref(feed_biomass.Elementary) || ref(drain_biomass.Elementary)  then
    tbs3:               test (0!=0) error "Don not connect Elementary globals to this unit!";
    endifl
```

# APPENDIX B: THE MOST RELEVANT MODELING ASSUMPTIONS

## MODELING ASSUMPTIONS

Here the most relevant modeling parameters (and some results such as fermentor size, efficiencies etc. ) are listed. For those unit operations that are only used in some production concepts, the enumerated concepts in which these assumptions are valid are listed in brackets next to the unit operation. All chemical conversions are given in % of substrate that is converted according to the respective products.

| | Straw | Softwood |
|---|---|---|
| **Size reduction** | | |
| Specific energy consumption | 36 kJ/kg | 36 kJ/kg |
| **Steam explosion** | | |
| $SO_2$ content (w/w% of dry biomass) | 1 w/w% | 2.5 w/w% |
| Temperature (two step pretreatment for softwood) | 190 °C | 190+210 °C |
| Conversions of chemical reactions (equations in section 2.3) | | |
| Hemicellulose → C5 and C6 Sugar (1) | 80% | 85% |
| Hemicellulose → Degradation products (3) | 15% | 10% |
| Cellulose → C6 Sugar (2) | 10% | 35% |
| Cellulose → Degradation products (4) | 2% | 5% |
| **Enzyme production** | | |
| Temperature | 30 °C | |
| Conversions of chemical reactions (equations in section 2.3) | | |
| Carbohydrate → Enzyme (10) | 35% | |
| Carbohydrate → Microorganism (12) | 10% | |
| Carbohydrate → $H_2O+CO_2$ (11) | 50% | |
| Enzyme yield $Y_{E/S}$[88] | 0.28 kg/kg | |
| Specific enzyme activity | 600 FPU/g | |
| **Yeast propagation** | | |
| Temperature | 30 °C | |
| Conversions of chemical reactions (equations section 2.3) | | |
| C6 Sugar → Yeast biomass (12) | 60% | |
| C6 Sugar→ $H_2O+CO_2$ (11) | 35% | |
| Yeast biomass yield $Y_{X/S}$[89] | 0.5 kg/kg | |
| **SSF, fermentation of C6 sugars only (concepts 1, 3, 4, 6, 7, 9-13)** | | |
| Initial water insoluble solid (WIS) content | 12 w/w% | 10 w/w% |
| Conversions of chemical reactions (equations section 2.3) | | |
| Cellulose → C6 Sugar (2) | 92% | |
| C6 Sugar → Bioethanol (6) | 92% | |

---

[88] *kg enzyme produced per kg substrate consumed*

[89] *kg yest produced per kg substrate consumed*

| | | |
|---|---|---|
| C5 Sugar → Bioethanol (7) | 0% | |
| Enzyme loading | 15 FPU/g Cellulose | |
| Initial yeast concentration | 2 g/l | |
| Residence time | 72 h | |
| Fermentor volume [90] | 22'600 $m^3$ | 20'100 $m^3$ |
| **SSCF, fermentation of C6+C5 sugars (concepts 2 & 5)** | | |
| Initial water insoluble solid (WIS) content | 12 w/w% | not applicable |
| Conversions of chemical reactions (equations section 2.3) | | |
| Cellulose → C6 Sugar (2) | 92% | |
| C6 Sugar → Bioethanol (6) | 92% | |
| C5 Sugar → Bioethanol (7) | 75% | |
| Enzyme loading | 15 FPU/g Cellulose | |
| Initial yeast concentration | 2 g/l | |
| Residence time | 72 h | |
| Fermentor volume | 15'620 $m^3$ | |
| **SSF, fermentation of C6 sugars at high water insoluble solid (WIS) content (concept 8)** | | |
| Initial water insoluble solid (WIS) content | 20 w/w% | not applicable |
| Conversions of chemical reactions (equations section 2.3) | | |
| Cellulose → C6 Sugar (2) | 92% | |
| C6 Sugar → Bioethanol (6) | 92% | |
| C5 Sugar → Bioethanol (7) | 0% | |
| Enzyme loading | 15 FPU/g Cellulose | |
| Initial yeast concentration | 3.5 g/l | |
| Residence time | 72 h | |
| Fermentor volume | 13'950 $m^3$ | |
| **Distillation and Pressure Swing Adsorption** | | |
| Pressure stripper 1 | 3 bar | |
| Pressure stripper 2 | 1.25 bar | |
| Pressure rectifyer | 0.35 bar | |
| Bioethanol recovery in each single column | 99.99 % | |
| Scecific elecricity demand PSA[91] | 30 kJ/kg | |
| Feed temperature PSA | 130 °C | |
| **Solid-Liquid separation and evaporation (concepts 1-9, 11, 12)** | | |
| Dry matter content of solids after filterpress | 45 w/w% | |
| Retention of insoluble solids | 99% | |
| Number of evaporation stages | 5 | |
| Steam quality (x) of vapors after heat exchange | 0 | |
| Dry matter content (total) of concentrate | 50 bzw. 65 w/w% | |
| ΔT Evaporation[92] | 10 °C | |
| **Anaerobic digestion, Up-grading, aerobic water treatment (concepts 10 & 13)** | | |
| COD concentration in the feed | 130 g/l | 40 g/l |
| Sulfur/COD in the feed | 7 g/kg | 42 g/kg |
| Conversions of chemical reactions (equations section 2.3) | | |
| Substrate → $CH_4 + CO_2 + H_2S$[93] (13) | 75% | 75% |
| Susbtrate → Anaerobic sludge | 15% | 15% |
| Methane yield | 263 $l_n$/kg COD | 258 $l_n$/kg COD |

---

[90] *Gas head volume and excess volume for cleaning etc. are not included.*

[91] *per kg of ethanol product, see section 2.3.8.2.*

[92] *Temperature differnce between heating steam and operating temperature.*

[93] *In section keine Reduktion von Schwefel angegeben. Bei den Berechnungen wird diese aber mitberücksichtigt.*

| | | |
|---|---|---|
| Specific sludge formation | 0.146 kg/kg COD | 0.153 kg/kg COD |
| Methane loss due to $H_2S$ formation | 0.2% | 3.0% |
| $H_2S$ in sour biogas | 0.76 vol% | 4.1 vol% |
| COD Organic loading rate | 20 kg/$m^3$d | |
| Residence time | 6.5 d | 2 d |
| Fermentor volume[94] | 48'800 $m^3$ | 13'000 $m^3$ |
| Max. sulfur content in PSA feed | 5 mg/$Nm^3$ | |
| Required $H_2S$ removal | 99.95% | 99.99% |
| Specific energy consumption PSA | 0.25 kWh/$Nm^3$ Feedgas | |
| Methane loss PSA | 3% | |
| Methane content product gas | 98 vol% | |
| Specific sludge formation aerobic stage | 0.5 kg/kg $COD_{removed}$ | |
| **Combustion and fluegas utilization** | | |
| Combustion temperature (hot gas) | 820 °C | |
| Fluegas temperature after heat exchange (cold gas) | 120 °C | |
| λ combustion | 1.7 | |
| Fluegas recirculation rate | 45-55% | |
| **District heat (concepts 3, 6, 9)** | | |
| Feed temperature | 110 °C | not applicable |
| Return temperature | 50 C | |
| **CHP plant, electricity & extraction of process steam (concepts 1, 2, 10, 11, 13)** | | |
| Primary steam | 650 °C, 63 bar | |
| Extraction steam HP | 20 bar | |
| Extraction steam MP | 4 bar | |
| Condensation conditions | 50 °C, 0.12 bar, x=0.95 | |
| Isentropic efficiency of turbine | 0.87 | |
| Mechanical efficiency turbine | 0.97 | |
| Mechanical efficiency generator | 0.97 | |
| Electrical efficiency generator | 0.97 | |
| **CHP plant, electricity, extraction, backpresureturbine for district heat (concept 3)** | | |
| Primary steam | 700 C, 63 bar | |
| Extraction steam, HP | 20 bar | |
| Extraction steam MP | 4 bar | |
| Condensation conditions | 120 C, 2 bar, x=1.1 | |
| Isentropic efficiency of turbine | 0.87 | |
| Mechanical efficiency turbine | 0.97 | |
| Mechanical efficiency generator | 0.97 | |
| Electrical efficiency generator | 0.97 | |

---

[94] *Gas head volume not included.*

# APPENDIX C: MASS AND ENERGY BALANCES OF THE PRODUCTION CONCEPTS

In the following the mass and energy balances of the concepts are listed. Mass balances are given in t/y, energy balances as energy flows in MW.

## *NO. 1 STRAW C6 ETHANOL & ELECTRICITY*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw, fresh (90% dry matter) | 15’990 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 44’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648’063 | [t/y] | In |
| SO2 | 5’832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12’970 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19’875 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’500 | [t/y] | In |
| Process water ethanol production | 452’647 | [t/y] | In |
| Fresh water steam geneneration | 222’872 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 26’977’516 | [t/y] | In |
| Cooling water CHP (20°C) | 27’758’097 | | In |
| Air (Combustion) | 4’097’520 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 544’303 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 26’977’516 | [t/y] | Out |
| Cooling water CHP (40 °C) | 27’758’097 | | Out |
| CO2 from bioreactors | 112’977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 714’704 | [t/y] | Out |
| Ash from combustion | 51’840 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 79.2 | [MWth] | |
| Process cooling demand | 78.3 | [MWth] | Out |
| Thermal power combustion | 251.1 | [MWth] | |
| Efficiency steam boiler | 88.4 | [%] | |
| Thermal power steam | 221.9 | [MWth] | |
| Electrical power generated | 57.5 | [MWel] | |
| Efficiency CHP | 54.5 | [%] | |
| Electricity process demand | 10.1 | [MWel] | |
| Electricity for export | 47.4 | [Mwel] | Out |
| Thermal power in fluegas (120 → 25 C) | 16.7 | [MWth] | Out |
| Cooling condensation CHP | 80.6 | [MWth] | Out |

| | | |
|---|---|---|
| Energy efficiency process | 39.2 | [%] |

## *No. 2 Straw C6 + C5 Ethanol & Electricity*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8'000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15'991 | [kJ/kg] | |
| LHV Ethanol | 26'900 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 72'000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 446'455 | [t/y] | In |
| SO2 | 4'018 | [t/y] | In |
| NH3 (28w/w% in H2O) | 8'938 | [t/y] | In |
| Beet molasses (80% DM) | 4'700 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 16'644 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2'094 | [t/y] | In |
| Process water ethanol production | 199'408 | [t/y] | In |
| Fresh water steam geneneration | 210'191 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 20'745'530 | [t/y] | In |
| Cooling water CHP (20 °C) | 12'880'723 | [t/y] | In |
| Air (Combustion) | 2'187'604 | [t/y] | In |
| Ethanol (100%) | 100'000 | [t/y] | Out |
| Waste water | 442'169 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 20'745'530 | [t/y] | Out |
| Cooling water CHP (40 °C) | 12'880'723 | [t/y] | Out |
| CO2 from bioreactors | 107'940 | [t/y] | Out |
| Ethanol in CO2 stream | 20 | [t/y] | Out |
| CO2 in fluegas | 381'570 | [t/y] | Out |
| Ash from combustion | 35'209 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 247.9 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 58.3 | [MWth] | |
| Process cooling demand | 60.2 | [MWth] | Out |
| Thermal power combustion | 145.1 | [MWth] | |
| Efficiency steam boiler | 88.2 | [%] | |
| Electrical power generated | 29.8 | [MWel] | |
| Thermal power steam | 127.9 | [MWth] | |
| Electricity process demand | 9.8 | [MWel] | |
| Thermal power in fluegas (120 → 25°C) | 8.3 | [MWth] | Out |
| Electricity for export | 20.0 | [MWel] | Out |
| Energy efficiency process | 44.0 | [%] | |

## *NO. 3 STRAW C6 ETHANOL. ELECTRICITY & DISTRICT HEAT*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’990 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 44’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 37 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648’063 | [t/y] | In |
| SO2 | 5’832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12’507 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19’875 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’500 | [t/y] | In |
| Process water ethanol production | 459’014 | [t/y] | In |
| Fresh water steam geneneration | 215’145 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 17’001’996 | [t/y] | In |
| Air (Combustion) | 4’088’071 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 543’059 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 17’001’996 | [t/y] | Out |
| CO2 from bioreactors | 112’977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 714’704 | [t/y] | Out |
| Ash from combustion | 49’706 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 79.1 | [MWth] | |
| Process cooling demand | 42.0 | [MWth] | Out |
| Thermal power combustion | 252.6 | [MWth] | |
| Efficiency steam boiler | 87.1 | [%] | |
| Thermal power steam | 220.0 | [MWth] | |
| Electrical power generated | 48.2 | [MWel] | |
| Efficiency CHP | 100.0 | [%] | |
| Electricity process demand | 10.1 | [MWel] | |
| Electricity for export | 38.1 | [Mwel] | Out |
| Thermal power in fluegas (120 →25 °C) | 18.6 | [MWth] | Out |
| Thermal power district heat (110 → 50 °C) | 125.3 | [MWth] | Out |
| Energy efficiency process | 71.4 | [%] | |

## *No. 4 Straw C6 Ethanol & Pellets*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8'000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15'990 | [kJ/kg] | |
| LHV Ethanol | 26'900 | [kJ/kg] | |
| *LHV Pellets. fresh (90% DM)* | 16'486 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 44'000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648'063 | [t/y] | In |
| SO2 | 5'832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12'507 | [t/y] | In |
| Beet molasses (80% DM) | 6'621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19'875 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2'500 | [t/y] | In |
| Process water ethanol production | 312'535 | [t/y] | In |
| Fresh water steam geneneration | 289'754 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 28'087'776 | [t/y] | In |
| Air (Combustion) | 1'509'984 | [t/y] | In |
| Ethanol (100%) | 100'000 | [t/y] | Out |
| Waste water | 572'818 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 28'087'776 | [t/y] | Out |
| CO2 from bioreactors | 112'977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 258'762 | [t/y] | Out |
| Ash from combustion | 14'005 | [t/y] | Out |
| Pellets (90% dry matter) | 272'353 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 81.8 | [MWth] | |
| Process cooling demand | 81.5 | [MWth] | Out |
| Thermal power combustion | 91.5 | [MWth] | |
| Efficiency steam boiler | 88.6 | [%] | |
| Thermal power steam | 81.1 | [MWth] | |
| Electricity process demand | 8.9 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 6.1 | [MWth] | Out |
| Energy flow Pellets | 155.9 | [MWth] | Out |
| Energy efficiency process | 67.6 | [%] | |

## *NO. 5 STRAW C6+C5 ETHANOL & PELLETS*

| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’990 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV Pellets. fresh (90% DM) | 17’690 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 72’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 446’455 | [t/y] | In |
| SO2 | 4’018 | [t/y] | In |
| NH3 (28w/w% in H2O) | 8’938 | [t/y] | In |
| Beet molasses (80% DM) | 4’700 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 16’644 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’094 | [t/y] | In |
| Process water ethanol production | 199’408 | [t/y] | In |
| Fresh water steam geneneration | 210’191 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 20’745’530 | [t/y] | In |
| Air (Combustion) | 990’449 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 442’169 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 20’745’530 | [t/y] | Out |
| CO2 from bioreactors | 107’940 | [t/y] | Out |
| Ethanol in CO2 stream | 20 | [t/y] | Out |
| CO2 in fluegas | 172’924 | [t/y] | Out |
| Ash from combustion | 17’335 | [t/y] | Out |
| Pellets (90% dry matter) | 120’684 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 247.9 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 58.2 | [MWth] | |
| Process cooling demand | 60.2 | [MWth] | Out |
| Thermal power combustion | 65.9 | [MWth] | |
| Efficiency steam boiler | 88.2 | [%] | |
| Thermal power steam | 58.1 | [MWth] | |
| Electricity process demand | 9.0 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 3.8 | [MWth] | Out |
| Energy flow Pellets | 74.1 | [MWth] | Out |
| Energy efficiency process | 65.2 | [%] | |

## *NO. 6 STRAW C6 ETHANOL. C5 MOLASSES & DISTRICT HEAT*

| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’990 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV Pellets. fresh (90% DM) | 16’635 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 44’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 37 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648’063 | [t/y] | In |
| SO2 | 5’832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12’507 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19’875 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’500 | [t/y] | In |
| Process water ethanol production | 312’535 | [t/y] | In |
| Fresh water steam geneneration | 289’987 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 17’353’276 | [t/y] | In |
| Air (Combustion) | 2’144’722 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 553’735 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 17’353’276 | [t/y] | Out |
| CO2 from bioreactors | 112’977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 367’232 | [t/y] | Out |
| Ash from combustion | 18’564 | [t/y] | Out |
| Pellets (90% dry matter) | 209’439 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 81.5 | [MWth] | |
| Process cooling demand | 42.8 | [MWth] | Out |
| Thermal power combustion | 129.6 | [MWth] | |
| Efficiency steam boiler | 88.6 | [%] | |
| Thermal power steam | 114.8 | [MWth] | |
| Electricity process demand | 8.9 | [MWel] | In |
| Energy flow district heat (110 → 50 °C) | 72.5 | [MWth] | Out |
| Thermal power in fluegas (120 → 25 °C) | 8.7 | [MWth] | Out |
| Energy flow Pellets | 121.0 | [MWth] | Out |
| Energy efficiency process | 77.8 | [%] | |

## *NO. 7 STRAW C6 ETHANOL. C5 MOLASSES & PELLETS*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’991 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV Pellets. fresh (90% DM) | 17’212 | [kJ/kg] | |
| LHV C5 Molasses. fresh (65%DM) | 11’400 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 40’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 694’616 | [t/y] | In |
| SO2 | 6’252 | [t/y] | In |
| NH3 (28w/w% in H2O) | 13’906 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 20’742 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’606 | [t/y] | In |
| Process water ethanol production | 346’700 | [t/y] | In |
| Fresh water steam geneneration | 327’027 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 24’286’939 | [t/y] | In |
| Air (Combustion) | 1’147’792 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 619’793 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 24’286’939 | [t/y] | Out |
| CO2 from bioreactors | 112’991 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 214’727 | [t/y] | Out |
| Ash from combustion | 19’863 | [t/y] | Out |
| Pellets (90% dry matter) | 99’732 | [t/y] | Out |
| C5 Molassese (65% dry matter) | 333’207 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 385.7 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 71.4 | [MWth] | |
| Process cooling demand | 70.5 | [MWth] | Out |
| Thermal power combustion | 80.8 | [MWth] | |
| Efficiency steam boiler | 88.3 | [%] | |
| Thermal power steam | 71.3 | [MWth] | |
| Electricity process demand | 8.5 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 4.4 | [MWth] | Out |
| Energy flow Pellets | 59.6 | [MWth] | Out |
| Energy flow C5 Molasses | 131.9 | [MWth] | Out |
| Energy efficiency process | 72.3 | [%] | |

## *No. 8 Straw C6HWIS Ethanol. C5 Molasses & Pellets*

| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8’000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’991 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV Pellets. fresh (90% DM) | 17’212 | [kJ/kg] | |
| LHV C5 Molasses. fresh (65%DM) | 11’400 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 40’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 694’616 | [t/y] | In |
| $SO_2$ | 6’252 | [t/y] | In |
| $NH_3$ (28w/w% in $H_2O$) | 13’906 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 20’742 | [t/y] | In |
| Diammoniumphosphate $(NH_4)_2HPO_4$ (DAP) | 2’606 | [t/y] | In |
| Process water ethanol production | 346’700 | [t/y] | In |
| Fresh water steam geneneration | 327’027 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 24’286’939 | [t/y] | In |
| Air (Combustion) | 1’147’792 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 619’793 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 24’286’939 | [t/y] | Out |
| $CO_2$ from bioreactors | 112’991 | [t/y] | Out |
| Ethanol in $CO_2$ stream | 23 | [t/y] | Out |
| $CO_2$ in fluegas | 214’727 | [t/y] | Out |
| Ash from combustion | 19’863 | [t/y] | Out |
| Pellets (90% dry matter) | 99’732 | [t/y] | Out |
| C5 Molassese (65% dry matter) | 333’207 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 385.7 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 71.4 | [MWth] | |
| Process cooling demand | 70.5 | [MWth] | Out |
| Thermal power combustion | 80.8 | [MWth] | |
| Efficiency steam boiler | 88.3 | [%] | |
| Thermal power steam | 71.3 | [MWth] | |
| Electricity process demand | 8.5 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 4.4 | [MWth] | Out |
| Energy flow Pellets | 59.6 | [MWth] | Out |
| Energy flow C5 Molasses | 131.9 | [MWth] | Out |
| Energy efficiency process | 72.3 | [%] | |

### *NO. 9 STRAW C6 ETHANOL. C5 MOLASSES & DISTRICT HEAT*

| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8000 | [h/y] | |
| LHV Straw. fresh (90% dry matter) | 15’991 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV C5 Molasses. fresh (65%DM) | 11’937 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 44’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 37 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648’063 | [t/y] | In |
| SO2 | 5’832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12’507 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19’874 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’499 | [t/y] | In |
| Process water ethanol production | 312’535 | [t/y] | In |
| Fresh water steam geneneration | 289’754 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 18’506’030 | [t/y] | In |
| Air (Combustion) | 1’861’424 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 553’734 | [t/y] | Out |
| Cooling water ethanol production (37 °C) | 18’506’030 | [t/y] | Out |
| CO2 from bioreactors | 112’977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 347’547 | [t/y] | Out |
| Ash from combustion | 35’130 | [t/y] | Out |
| C5 Molassese (65% dry matter) | 295’153 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 81.5 | [MWth] | |
| Process cooling demand | 45.7 | [MWth] | Out |
| Thermal power combustion | 129.4 | [MWth] | |
| Efficiency steam boiler | 88.1 | [%] | |
| Thermal power steam | 114.0 | [MWth] | |
| Electricity process demand | 8.9 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 7.1 | [MWth] | Out |
| Energy flow District heat | 68.9 | [MWth] | Out |
| Energy flow C5 Molasses | 122.0 | [MWth] | Out |
| Energy efficiency process | 77% | [%] | |

## *No. 10 Straw C6 Ethanol. Biomethane & Electricity*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8000 | [h/y] | |
| LHV Straw fresh (90% dry matter) | 15’991 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| LHV Biomethane 98vol% | 47’537 | [kJ/kg] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| **Mass balance** | | | |
| Straw (fresh) | 648’063 | [t/y] | In |
| SO2 | 5’832 | [t/y] | In |
| NH3 (28w/w% in H2O) | 12’507 | [t/y] | In |
| Beet molasses (80% DM) | 6’621 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 19’874 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’499 | [t/y] | In |
| Phosphoric Acid H3PO4 (100%) | 437 | [t/y] | In |
| Process water ethanol production | 2’020’772 | [t/y] | In |
| Fresh water steam geneneration | 289’895 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 23’538’781 | [t/y] | In |
| Cooling water CHP (20 °C) | 8’414’089 | [t/y] | In |
| Air (Combustion and water treatment) | 2’515’141 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| BioCH4 (98vol%) | 62’259 | [t/y] | Out |
| BioCH4 (98vol%) | 84.5 | [Mio. $Nm^3$/a] | Out |
| Water leaving water treatment | 2’187’017 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 23’538’781 | [t/y] | Out |
| Cooling water CHP (40 °C) | 8’414’090 | [t/y] | Out |
| Biological Sulfur | 1’710 | [t/y] | Out |
| CO2 from bioreactors | 112’977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 469’944 | [t/y] | Out |
| CO2 generated in water treatment | 33’033 | [t/y] | Out |
| Ash from combustion | 30’081 | [t/y] | Out |
| Sludge (anaerobic+ aerobic)(30%DM) | 185’273 | [t/y] | Out |
| Sludge (anaerobic+ aerobic)(75%DM) | 74’109 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Straw | 359.6 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Energy flow BioCH4 | 102.8 | [MWch] | Out |
| Process heat demand | 66.2 | [MWth] | |
| Process cooling demand | 68.2 | [MWth] | Out |
| Thermal power combustion | 133.2 | [MWth] | |
| Efficiency steam boiler | 88.2 | [%] | |
| Thermal power process steam | 117.5 | [MWth] | |
| Electrical power generated | 24.8 | [MWel] | |
| Efficiency CHP | 68.3 | [%] | |
| Electricity process demand | 15.1 | [$MW_{el}$] | |
| Electricity for export | 9.7 | [$MW_{el}$] | Out |
| Thermal power in fluegas (120 → 25 °C) | 7.8 | [$MW_{el}$] | Out |
| Cooling power condensation CHP | 24.4 | [$MW_{el}$] | Out |
| Energy efficiency process | 57.3 | [%] | |

## *NO. 11 SOFTWOOD C6 ETHANOL & ELECTRICITY*

| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8000 | [h/y] | |
| LHV Softwood, fresh (45% dry matter) | 7’254 | [kJ/kg] | |
| LHV Ethanol | 26’900 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 20’000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Softwood (fresh) | 868’599 | [t/y] | In |
| SO2 | 9’772 | [t/y] | In |
| NH3 (28w/w% in H2O) | 13’898 | [t/y] | In |
| Beet molasses (80% DM) | 6’968 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 18’538 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2’330 | [t/y] | In |
| Process water ethanol production | 243’629 | [t/y] | In |
| Fresh water steam geneneration | 239’281 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 26’369’652 | [t/y] | In |
| Cooling water CHP (20 °C) | 12’894’025 | | In |
| Air (Combustion) | 2’253’466 | [t/y] | In |
| Ethanol (100%) | 100’000 | [t/y] | Out |
| Waste water | 924’212 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 26’369’652 | [t/y] | Out |
| Cooling water CHP (40 °C) | 12’894’025 | [t/y] | Out |
| CO2 from bioreactors | 107’452 | [t/y] | Out |
| Ethanol in CO2 stream | 21 | [t/y] | Out |
| CO2 in fluegas | 423’821 | [t/y] | Out |
| Ash from combustion | 25’236 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Softwood | 218.8 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 69.2 | [MWth] | |
| Process cooling demand | 68.4 | [MWth] | Out |
| Thermal power combustion | 160.5 | [MWth] | |
| Efficiency steam boiler | 88.5 | [%] | |
| Thermal power steam | 142.1 | [MWth] | |
| Electrical power generated | 32.8 | [MWel] | |
| Efficiency CHP | 63.5 | [%] | |
| Electricity process demand | 10.8 | [MWel] | |
| Electricity for export | 22.0 | [Mwel] | Out |
| Thermal power in fluegas (120 → 25 °C) | 8.7 | [MWth] | Out |
| Cooling condensation CHP | 37.4 | [MWth] | Out |
| Energy efficiency process | 52.7 | [%] | |

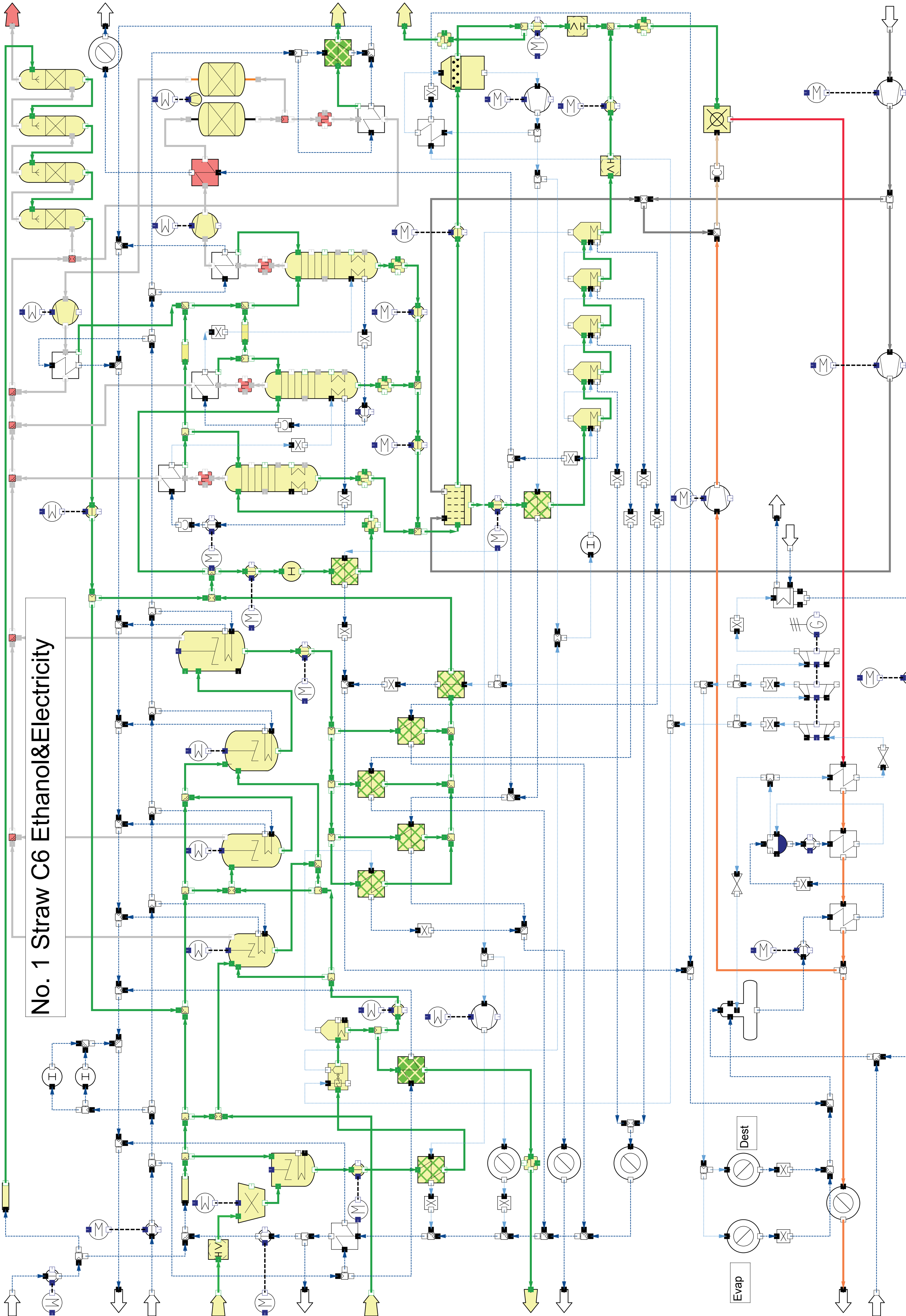
## *No. 12 Softwood C6 Ethanol & Pellets*

| Operating parameters | Value | Unit | In / Out |
|---|---|---|---|
| Online time | 8'000 | [h/y] | |
| LHV Softwood, fresh (45% dry matter) | 7'254 | [kJ/kg] | |
| LHV Ethanol | 26'900 | [kJ/kg] | |
| LHV Pellets, fresh (90% DM) | 19'551 | [kJ/kg] | |
| Chemical Oxygen Demand (COD) of waste water | 20'000 | [mg/l] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| Temperature waste water | 50 | [°C] | |
| **Mass balance** | | | |
| Softwood (fresh) | 868'599 | [t/y] | In |
| SO2 | 9'772 | [t/y] | In |
| NH3 (28w/w% in H2O) | 13'898 | [t/y] | In |
| Beet molasses (80% DM) | 6'968 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 18'538 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2'330 | [t/y] | In |
| Process water ethanol production | 243'629 | [t/y] | In |
| Fresh water steam geneneration | 239'281 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 26'369'652 | [t/y] | In |
| Cooling water CHP (20 °C) | 12'894'025 | [t/y] | In |
| Air (Combustion) | 1'120'392 | [t/y] | Out |
| Ethanol (100%) | 100'000 | [t/y] | Out |
| Waste water | 924'212 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 26'369'652 | [t/y] | Out |
| CO2 from bioreactors | 107'452 | [t/y] | Out |
| Ethanol in CO2 stream | 21 | [t/y] | Out |
| CO2 in fluegas | 209'496 | [t/y] | Out |
| Pellets (90% dry matter) | 113'697 | [t/y] | Out |
| Ash from combustion | 15'224 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Softwood | 218.8 | [MWch] | In |
| Energy flow Ethanol | 93.4 | [MWch] | Out |
| Process heat demand | 69.2 | [MWth] | |
| Process cooling demand | 68.4 | [MWth] | Out |
| Thermal power combustion | 78.1 | [MWth] | |
| Efficiency steam boiler | 88.6 | [%] | |
| Electricity process demand | 9.9 | [MWel] | In |
| Thermal power in fluegas (120 → 25 °C) | 4.4 | [MWth] | Out |
| Energy flow Pellets | 77.2 | [MWch] | Out |
| Energy efficiency process | 74.6 | [%] | |

## *No. 13 Softwood C6 Ethanol, Biomethane & Electricity*

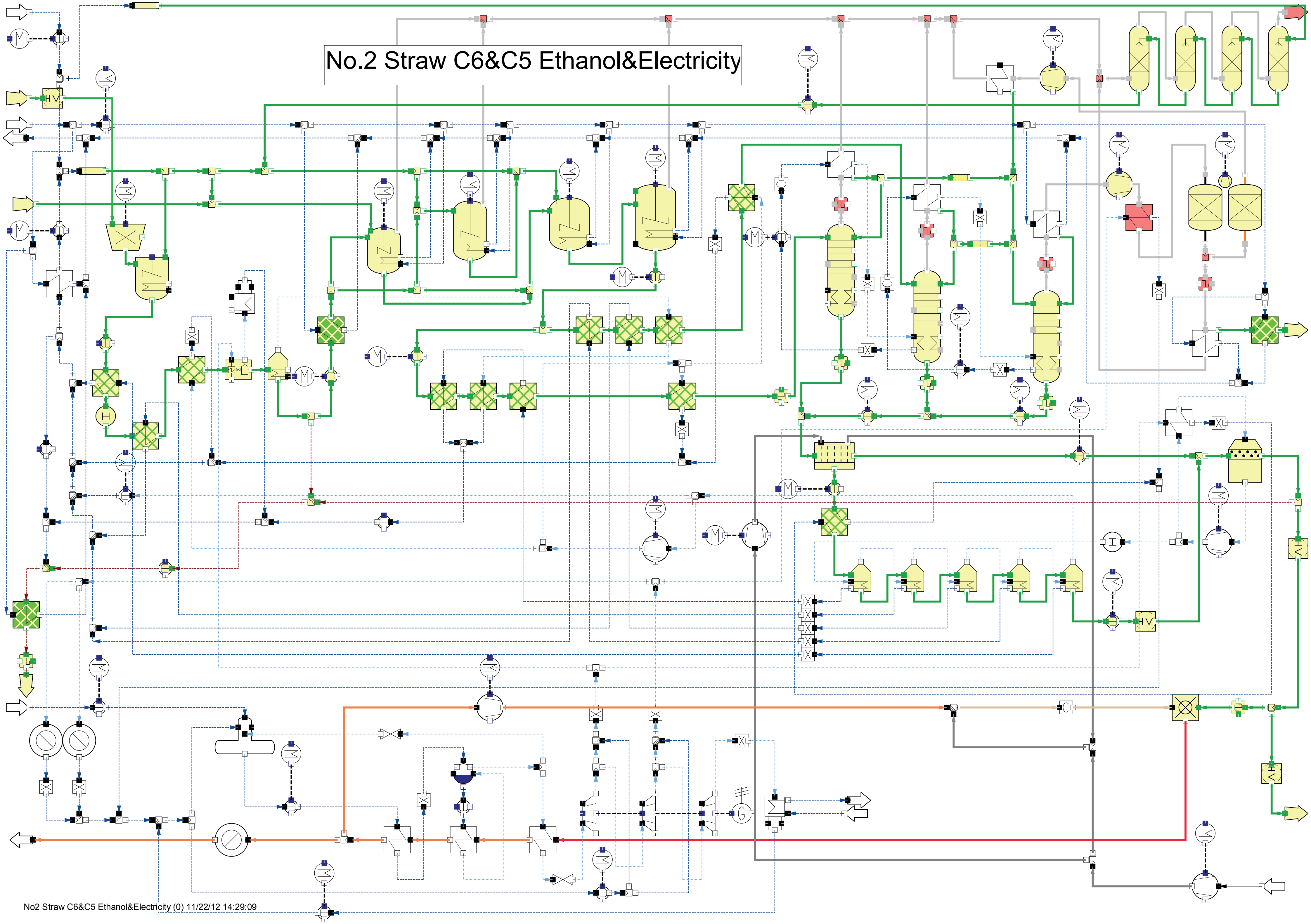
| **Operating parameters** | **Value** | **Unit** | **In / Out** |
|---|---|---|---|
| Online time | 8'000 | [h/y] | |
| LHV Softwood fresh (90% dry matter) | 7'254 | [kJ/kg] | |
| LHV Ethanol | 26'900 | [kJ/kg] | |
| LHV Biomethane 98vol% | 47'846 | [kJ/kg] | |
| Cooling water inlet temperature | 20 | [°C] | |
| Cooling water outlet temperature | 40 | [°C] | |
| **Mass balance** | | | |
| Softwood (fresh) | 868'599 | [t/y] | In |
| SO2 | 9'772 | [t/y] | In |
| NH3 (28w/w% in H2O) | 13'898 | [t/y] | In |
| Beet molasses (80% DM) | 6'968 | [t/y] | In |
| Corn Steep Liquor (CSL) (50%DM) | 18'538 | [t/y] | In |
| Diammoniumphosphate (NH4)2HPO4 (DAP) | 2'330 | [t/y] | In |
| Phosphoric Acid H3PO4 (100%) | 406 | [t/y] | In |
| Process water ethanol production | 1'442'863 | [t/y] | In |
| Fresh water steam geneneration | 239'279 | [t/y] | In |
| Cooling water ethanol production (20 °C) | 18'763'842 | [t/y] | In |
| Cooling water CHP (20 °C) | 10'655'902 | [t/y] | In |
| Air (Combustion and water treatment) | 1'926'789 | [t/y] | In |
| Ethanol (100%) | 100'000 | [t/y] | Out |
| BioCH4 (98vol%) | 16'491 | [t/y] | Out |
| BioCH4 (98vol%) | 23 | [Mio. $Nm^3$/a] | Out |
| Water leaving water treatment | 2'085'814 | [t/y] | Out |
| Cooling water ethanol production (40 °C) | 18'763'842 | [t/y] | Out |
| Cooling water CHP (40 °C) | 10'655'902 | [t/y] | Out |
| Biological Sulfur | 2'684 | [t/y] | Out |
| CO2 from bioreactors | 112'977 | [t/y] | Out |
| Ethanol in CO2 stream | 23 | [t/y] | Out |
| CO2 in fluegas | 363'491 | [t/y] | Out |
| CO2 generated in water treatment | 17'021 | [t/y] | Out |
| Ash from combustion | 7'866 | [t/y] | Out |
| Sludge (anaerobic+ aerobic)(30%DM) | 49'798 | [t/y] | Out |
| Sludge (anaerobic+ aerobic)(75%DM) | 19'919 | [t/y] | Out |
| **Energy balance** | | | |
| Energy flow Softwood | 218.8 | | In |
| Energy flow Ethanol | 93.4 | | Out |
| Energy flow BioCH4 | 27.4 | | Out |
| Process heat demand | 56.4 | | |
| Process cooling demand | 52.8 | | Out |
| Thermal power combustion | 130.3 | | |
| Efficiency steam boiler | 89% | | |
| Thermal power process steam | 115.7 | | |
| Electrical power generated | 26.2 | | |
| Efficiency CHP | 63% | | |
| Electricity process demand | 12.0 | | |
| Electricity for export | 14.2 | | Out |
| Thermal power in fluegas (120 → 25 °C) | 6.8 | | Out |
| Cooling power condensation CHP | 30.9 | | Out |
| Energy efficiency process | 61.7 | | |

# APPENDIX D: IPSEPRO FLOWSHEETS

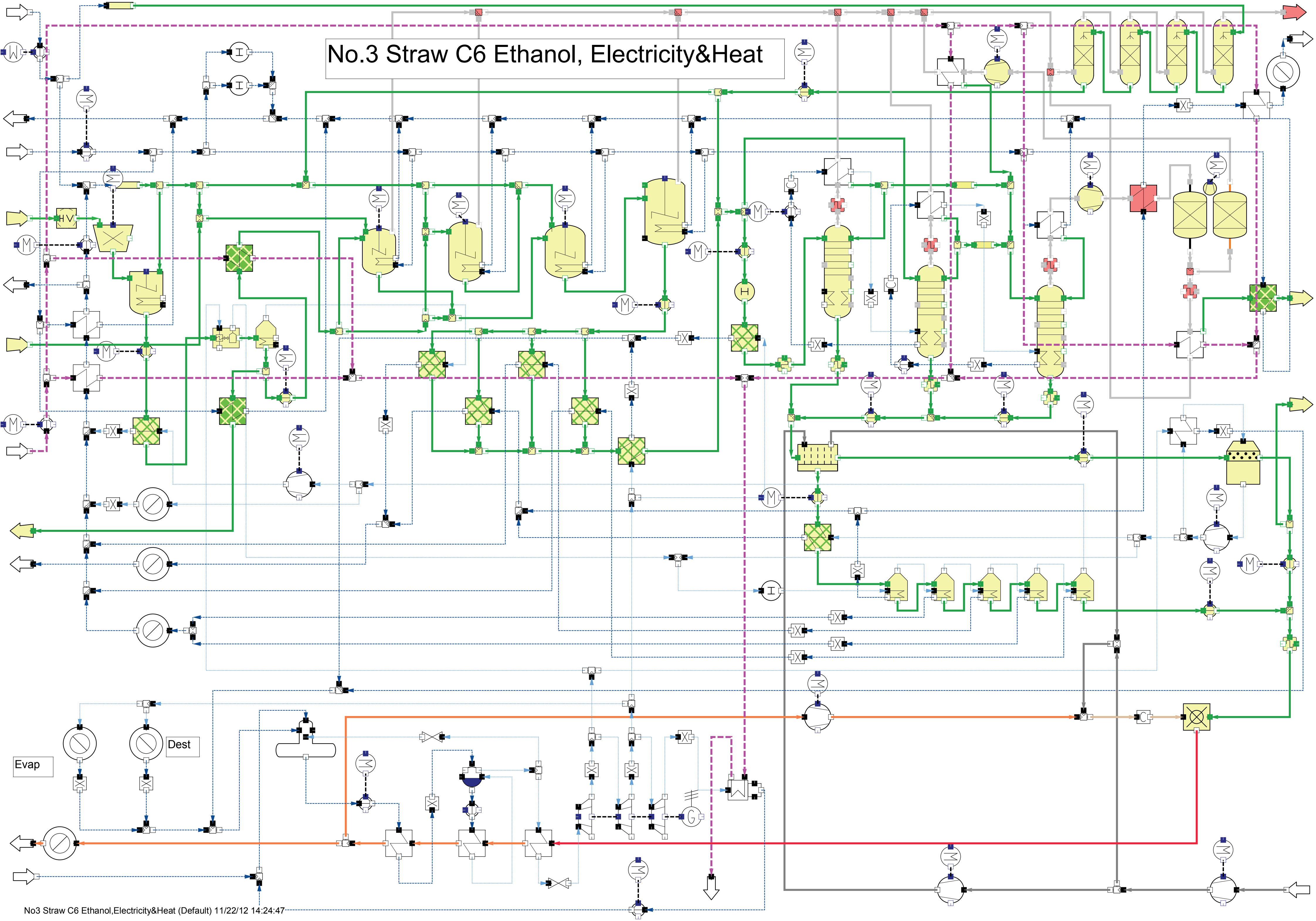


No1 Straw C6 Ethanol&Electricity (Default) 11/22/12 14:01:30

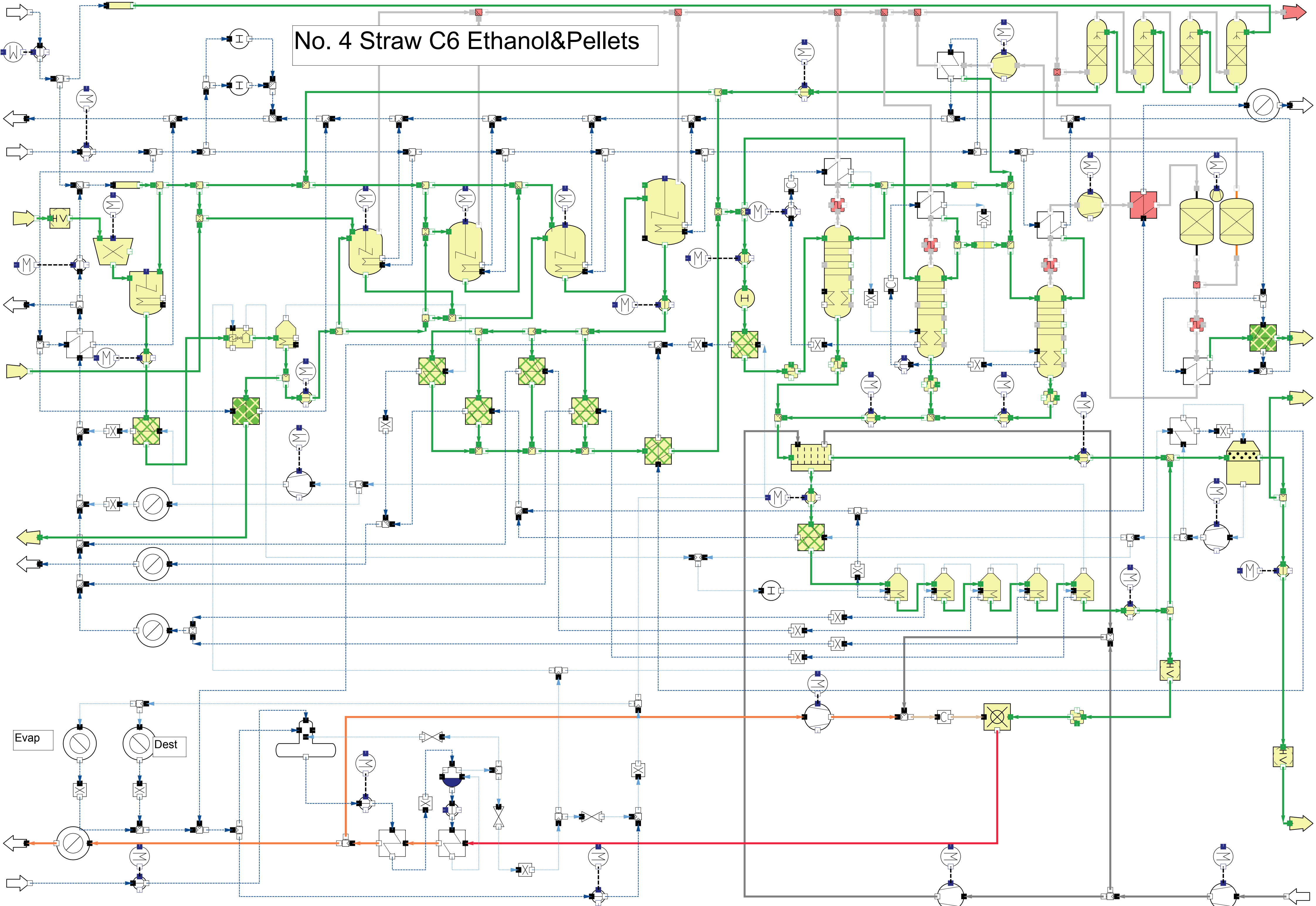
# No.2 Straw C6&C5 Ethanol&Electricity



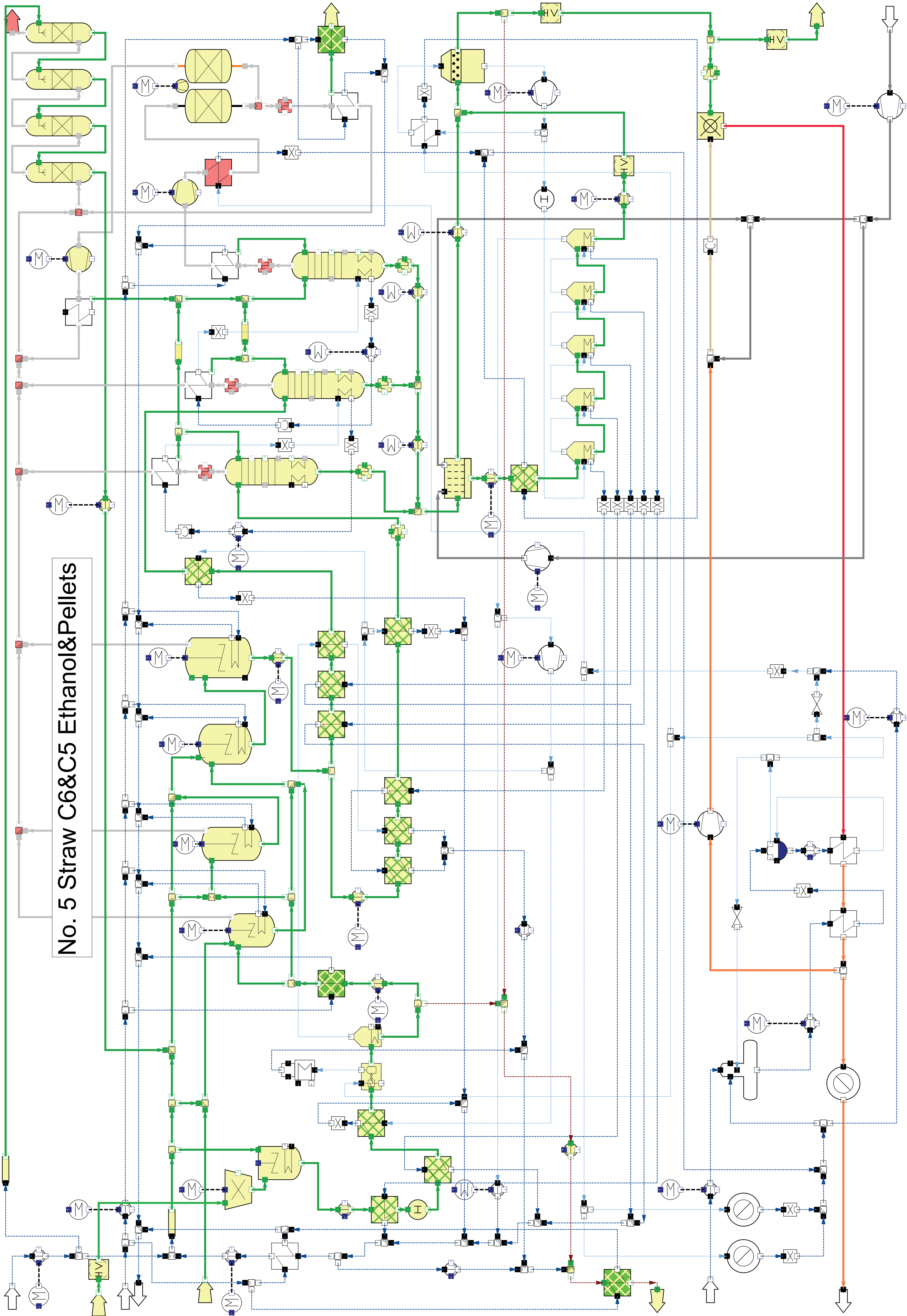
No2 Straw C6&C5 Ethanol&Electricity (0) 11/22/12 14:29:09


No.3 Straw C6 Ethanol, Electricity&Heat
Dest
Evap
No3 Straw C6 Ethanol,Electricity&Heat (Default) 11/22/12 14:24:47

# No. 4 Straw C6 Ethanol&Pellets

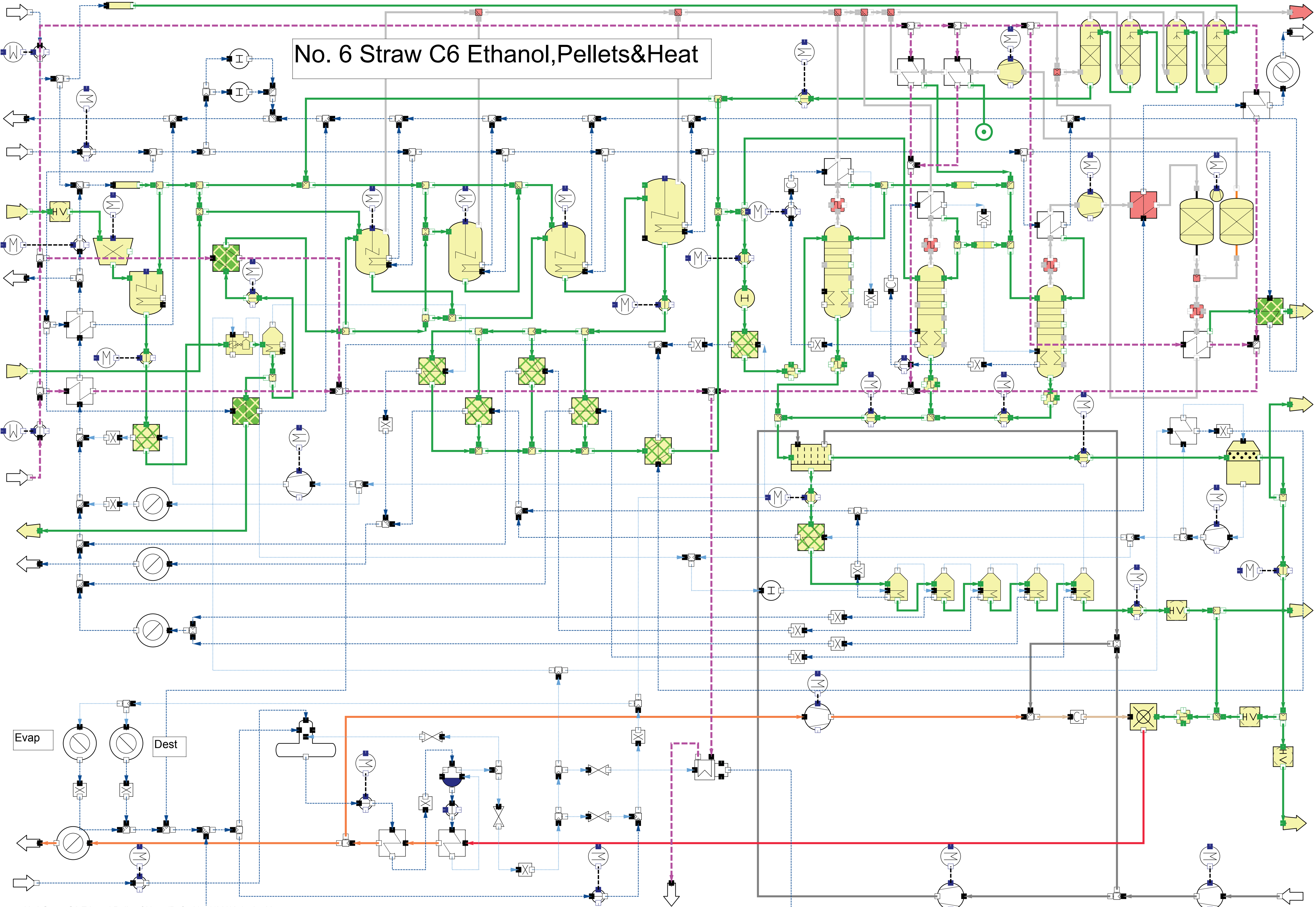


No4 Straw C6 Ethanol&Pellets (Default) 11/22/12 14:25:09


No. 5 Straw C6&C5 Ethanol&Pellets

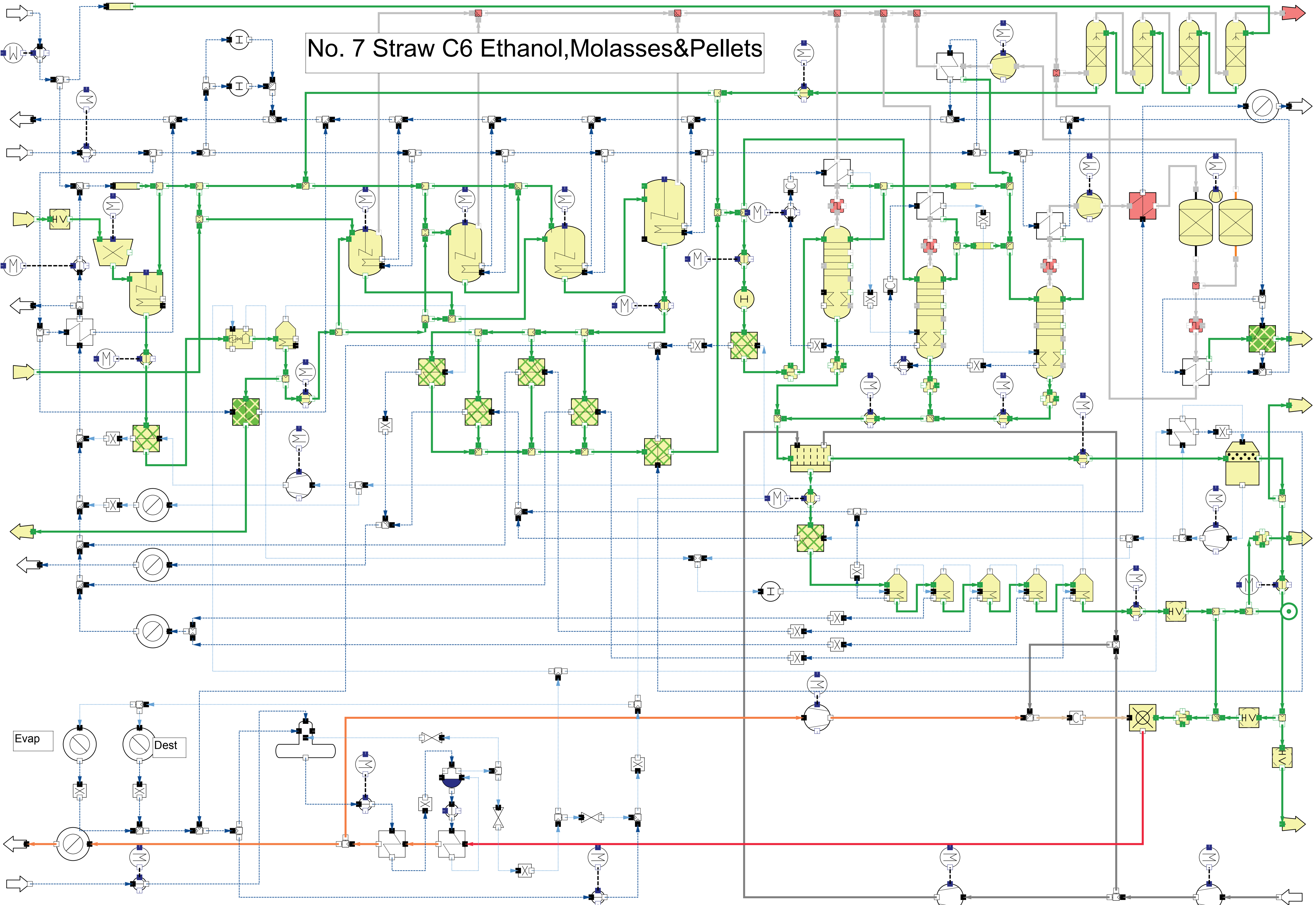
No5 Straw C6&C5 Ethanol&Pellets (Default) 11/22/12 14:32:14

# No. 6 Straw C6 Ethanol,Pellets&Heat

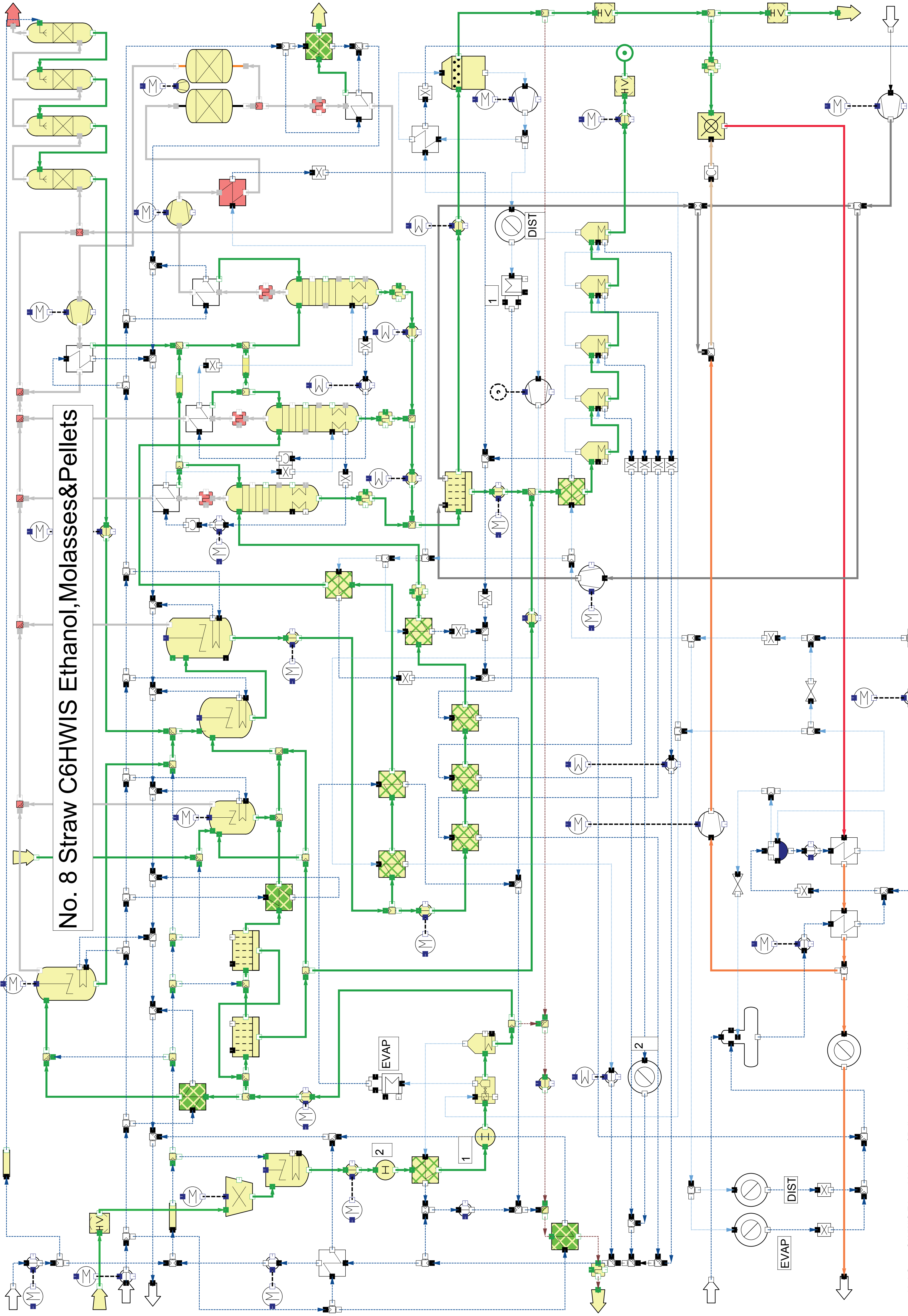


No6 Straw C6 Ethanol,Pellets&Heat (Default) 11/22/12 14:34:23

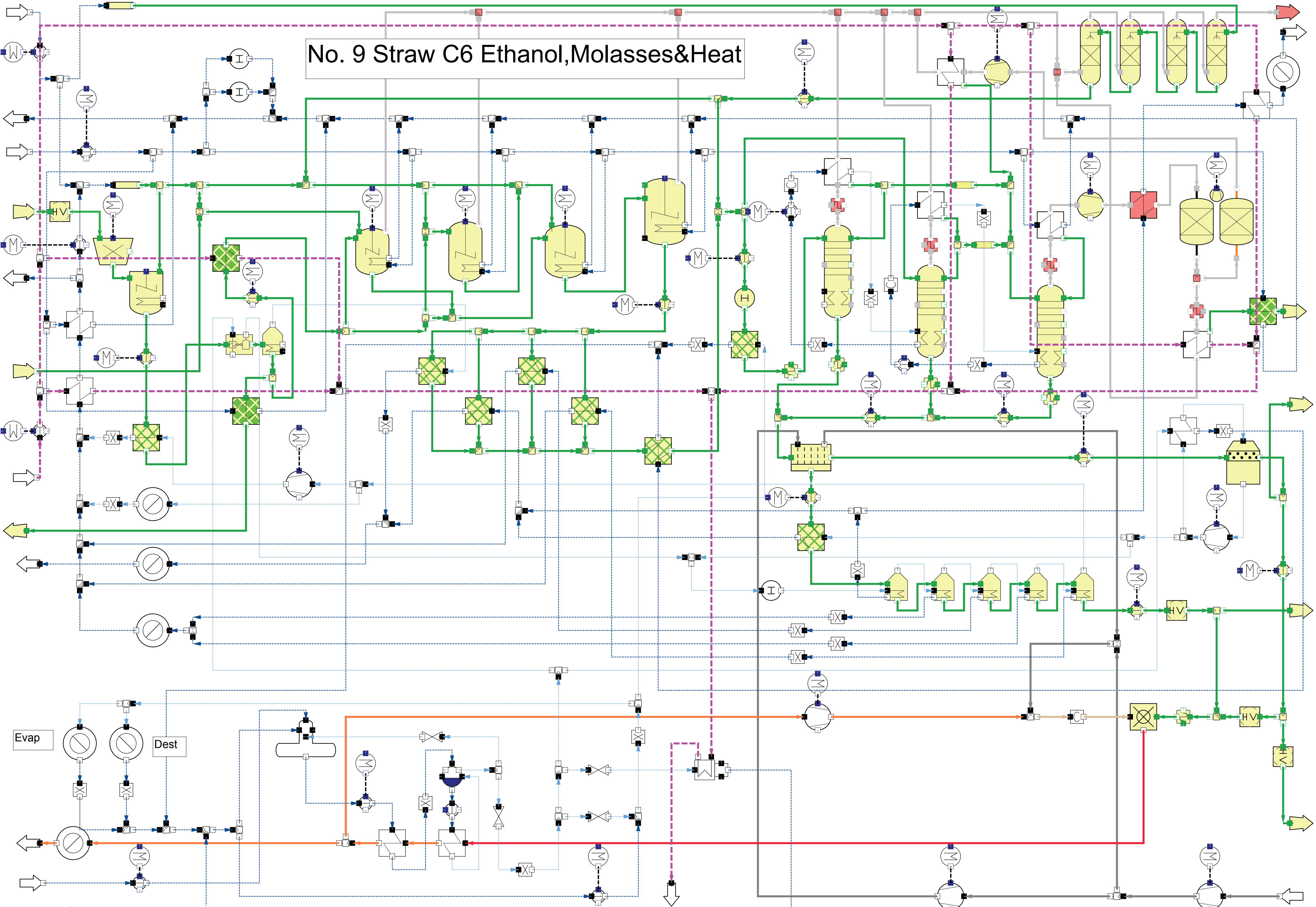
# No. 7 Straw C6 Ethanol,Molasses&Pellets



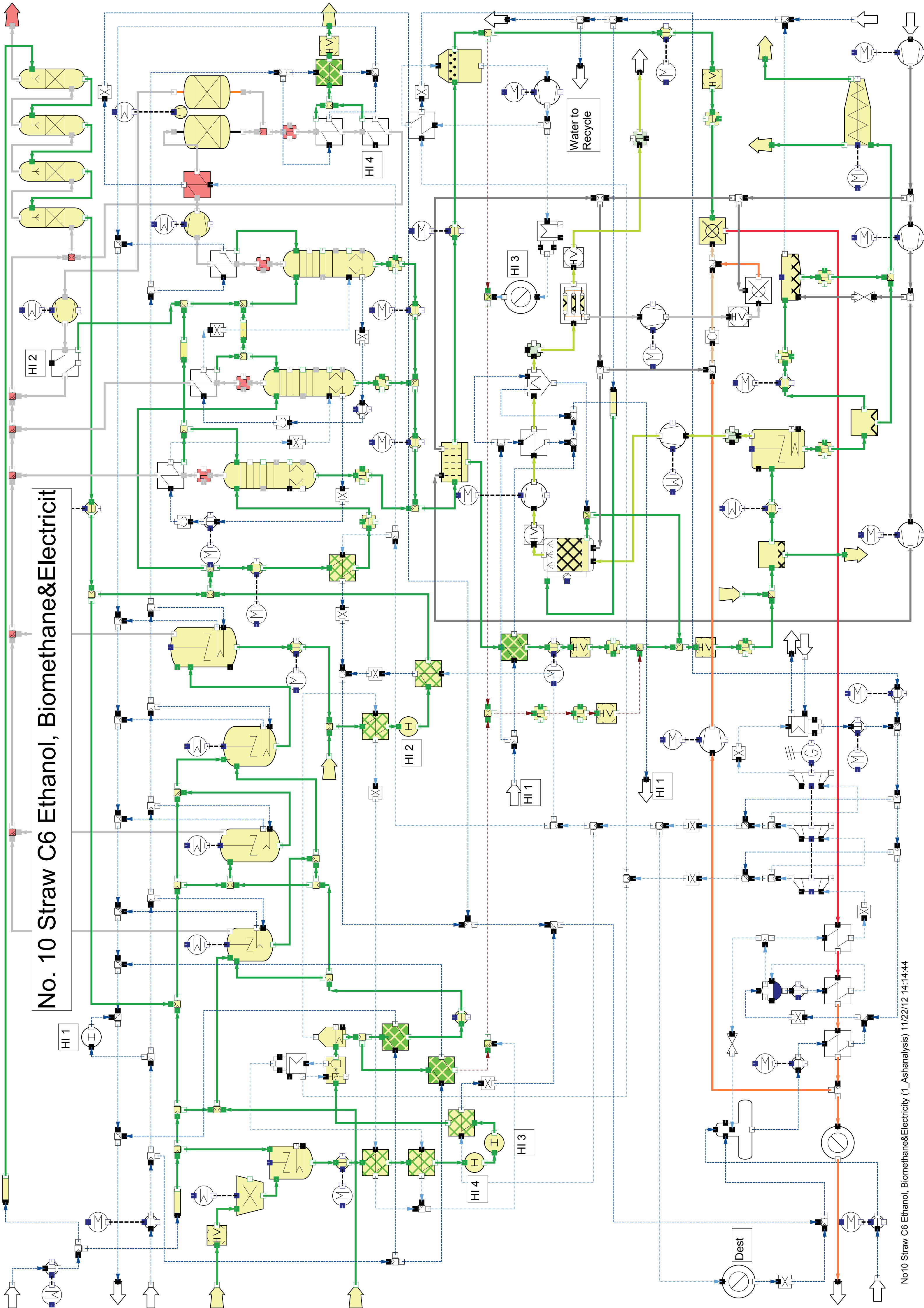
No7 Straw C6 Ethanol,Molasses&Pellets (Default) 11/22/12 14:37:19



No8 Straw C6HWIS Ethanol,Molasses&Pellets (variante1) 11/22/12 14:40:33

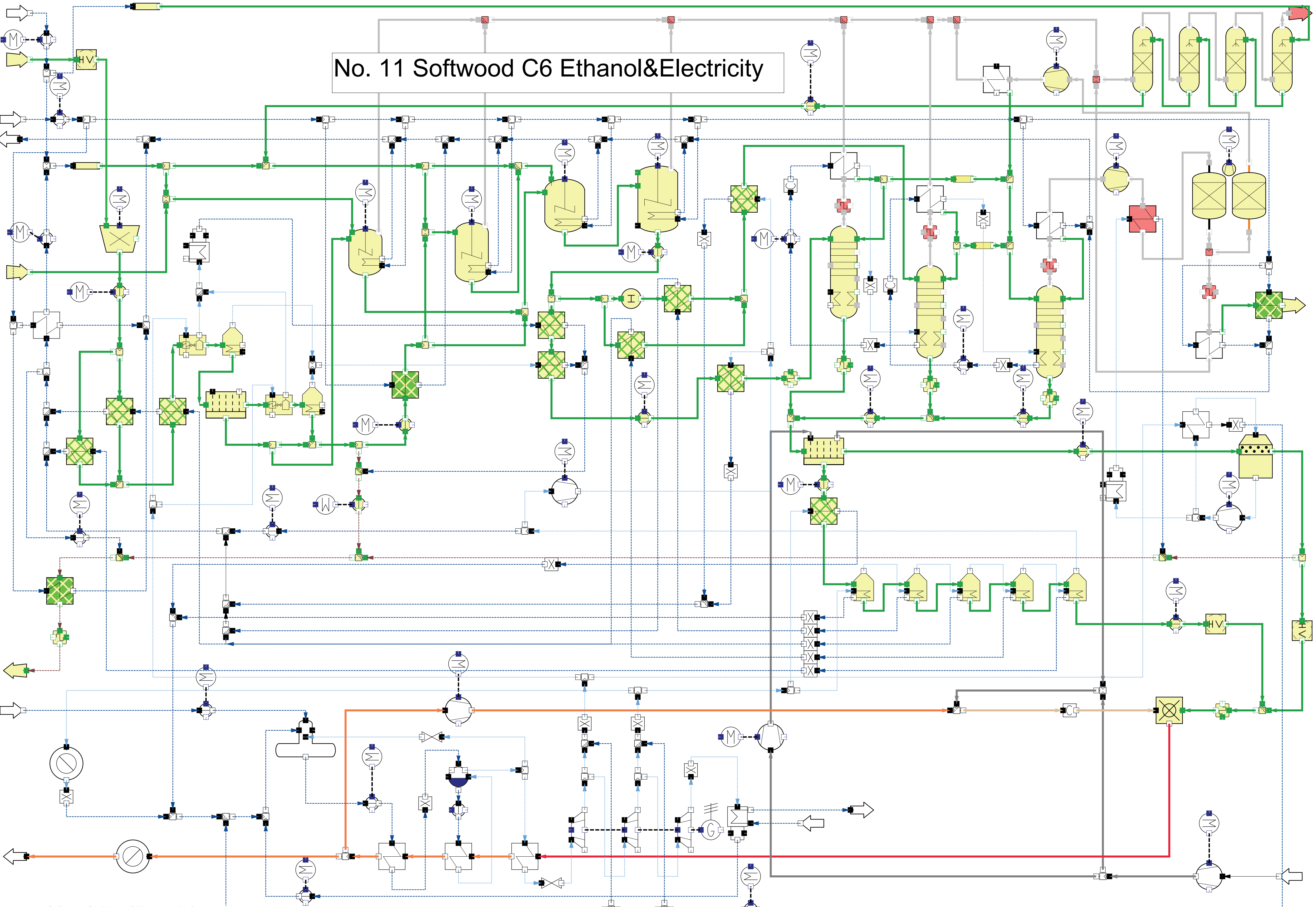


No9 Straw C6 Ethanol,Molasses&Heat (Default) 11/22/12 14:45:45


No. 10 Straw C6 Ethanol, Biomethane&Electricit

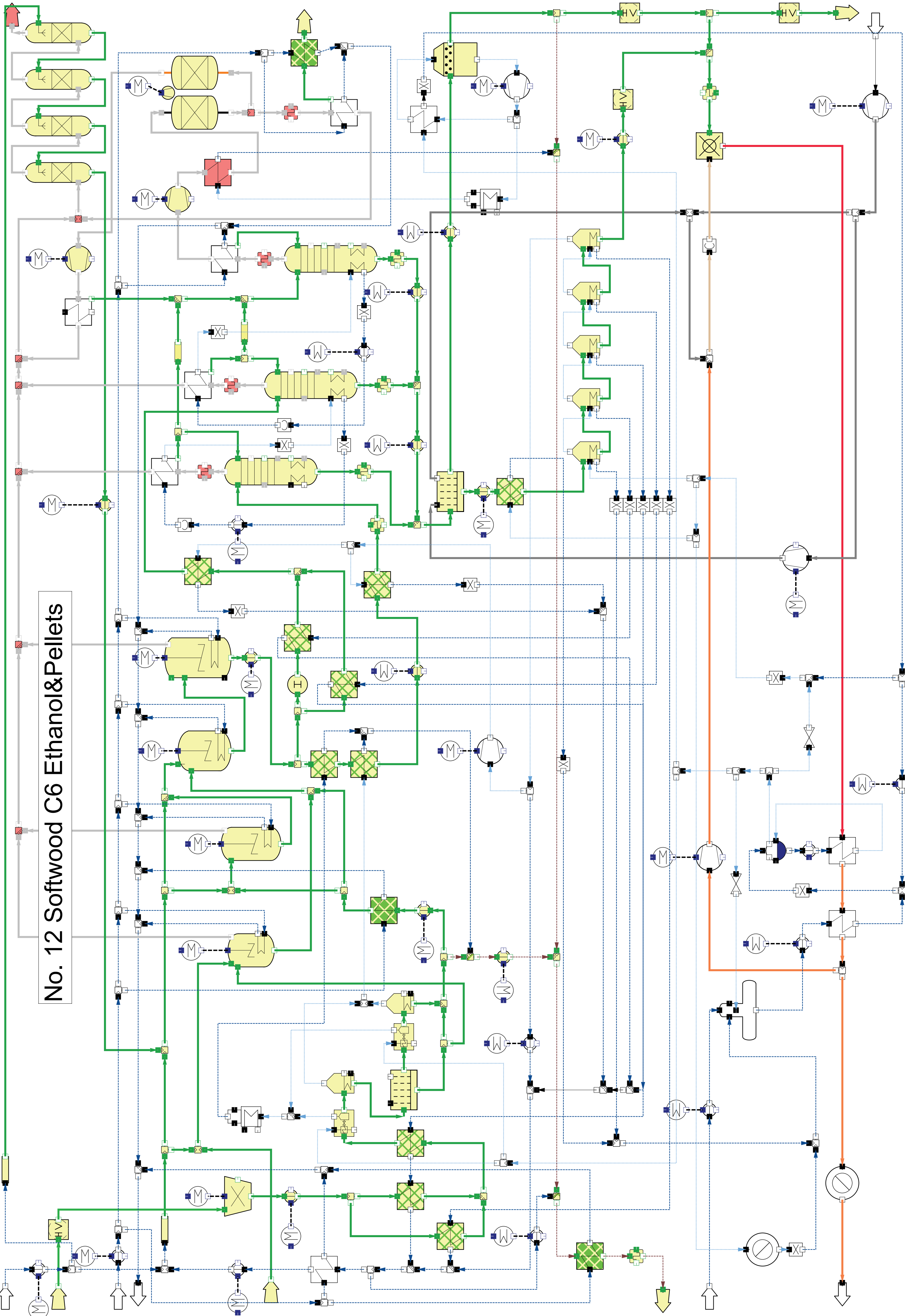
No10 Straw C6 Ethanol, Biomethane&Electricity (1_Ashanalysis) 11/22/12 14:14:44

# No. 11 Softwood C6 Ethanol&Electricity

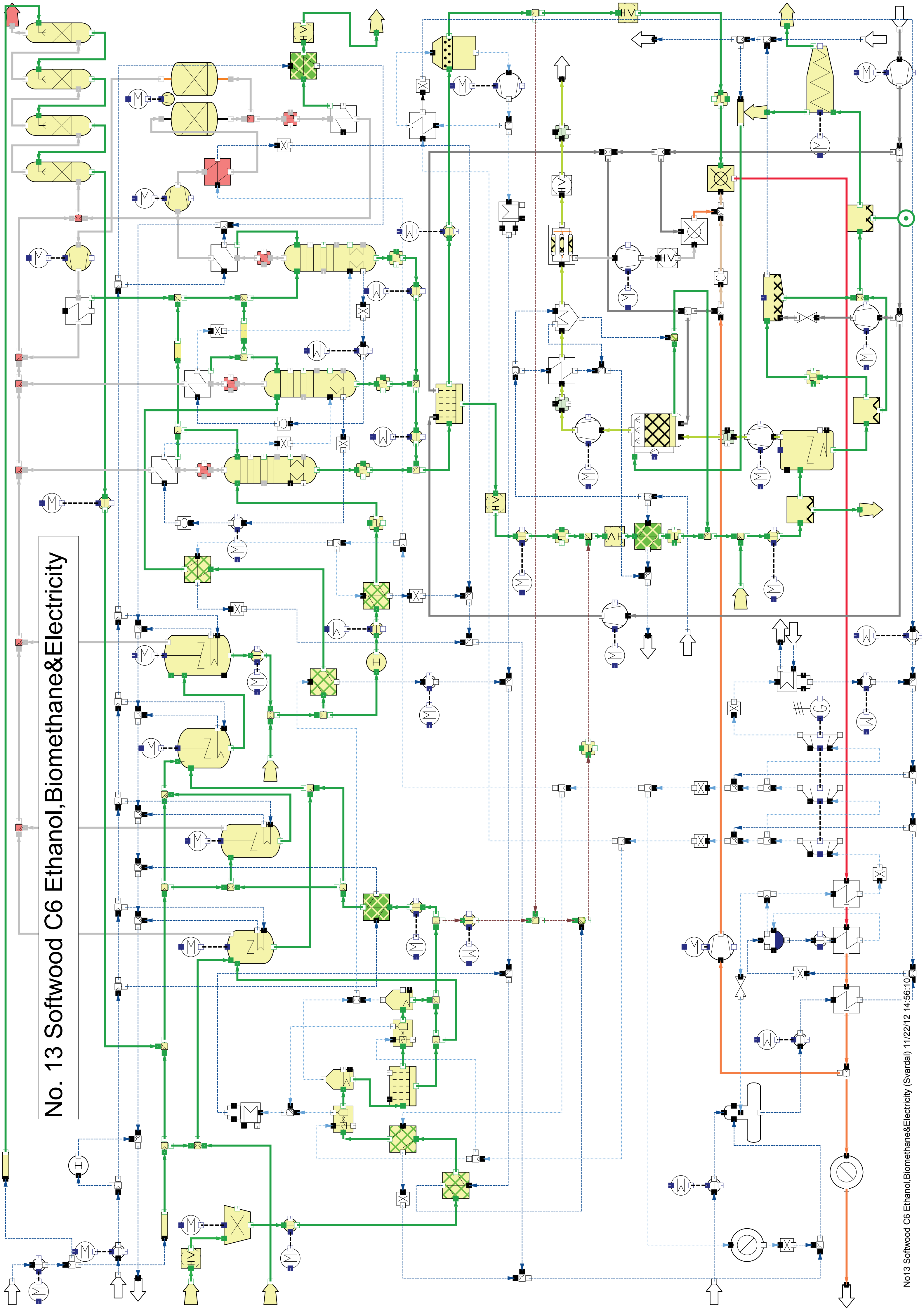


No11 Softwood C6 Ethanol&Electricity (Default) 11/22/12 14:49:02

# No. 12 Softwood C6 Ethanol&Pellets



No12 Softwood C6 Ethanol&Pellets (Default) 11/22/12 14:51:58


No. 13 Softwood C6 Ethanol,Biomethane&Electricity
No13 Softwood C6 Ethanol,Biomethane&Electricity (Svardal) 11/22/12 14:56:10
M
W
HV
H
G

# DI Philipp Kravanja

## Zur Person

| | |
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| Telefon | +43/664/4345276 |
| Geboren am | 25.09.1980 in Zell am See |
| Familienstand | verheiratet mit Mag. Vera Kravanja |
| Staatsbürgerschaft | Österreich |

## Ausbildung

| | |
|---|---|
| 03/2009 – 01/2013 | **Technische Universität Wien**<br>Doktoratsstudium der techn. Wissenschaften:**Verfahrenstechnik**<br>Doktorarbeit: Bioethanol production from lignocellulosic biomass – Process simulation and validation |
| 10/2001 – 01/2009 | **Technische Universität Wien**<br>Diplomstudium: **Technische Chemie**<br>Schwerpunkt: **Chemische Prozess – und Umwelttechnik**<br>Mit Auszeichnung abgeschlossen<br>Diplomarbeit: Cold flow studies in a stationary gas solid fluidized bed |
| 11/2007 – 06/2008 | **University of California, San Diego, USA**<br>Visiting scholar: Experimentelle Untersuchungen für Diplomarbeit |
| 02/2005 – 06/2005 | **Università di Bologna, IT**<br>Auslandssemester: Vorlesungen aus technischer Chemie und Vertiefung der Sprachkenntnisse |
| 10/2000 – 06/2001 | **Technische Universität Wien**<br>Diplomstudium Raumplanung, abgebrochen |
| 06/1999 | **BRG Braunau am Inn,** Matura mit gutem Erfolg |

## Berufserfahrung & Praktika

| | |
|---|---|
| 03/2009 – heute | **Technische Universität Wien**<br>wissenschaftlicher Mitarbeiter im Forschungsbereich Thermische Verfahrenstechnik und Prozeßsimulation (Prof. Anton Friedl)<br>bearbeitete Projekte:<br>• Bilanzierung und Evaluierung der kombinierten Herstellung von Bioethanol und Biogas aus Zuckerhirse (11/2011 – 06/2012). Partner: **EVM & BOKU**<br>• Prozeßentwicklung und Bilanzierung einer Strohbioraffinerie (04/2010 – 09/2010). Partner: **Annikki GmbH**<br>• Prozeßsimulation der Biogasproduktion aus vorbehandeltem Stroh (03/2010 – 06/2012). Partner: **Biogest GmbH & Profactor GmbH** |

| | |
|---|---|
| | • Prozeßsimulation der Bioethanolproduktion aus Holz und Stroh (03/2009 – 06/2011). Partner: **Joanneum Research**<br>• Evaluierung von Simulationstools für die Roheisenerzeugung (08/2009 – 03/2010). Auftraggeber: **Siemens VAI** |
| 06/2007 & 07/2007 | **Technische Universität Wien & Vogelbusch GmbH**<br>Praktikum: CFD Simulation der Strömung in T-Stücken |
| 02/2006 & 06/2006 | **Christian Doppler Labor für Mycotoxin-Forschung, Tulln**<br>Praktikum: HPLC Analyse von Mycotoxinen, Methodenentwicklung und Durchführung |
| 08/2004 | **Initiative Dritte Welt**<br>Projektarbeit in Guatemala.<br>Thema: Gewinnung von Indigo aus Indigofera guatemalensis, Experimente zur Extraktion und Abtrennung |
| während des Studiums | **Austria Alu Guss**, **Austria Metall AG, Wacker Chemie**<br>Ferialarbeit in der Produktion diverser Industriebetriebe |

## Fähigkeiten und Kompetenzen

| | |
|---|---|
| Fachkenntnisse | >3 Jahre Erfahrung in der Entwicklung, Simulation, Bilanzierung und Analyse biotechnologischer Prozesse, Modellentwicklung, Prozeßintegration, Pinch Analyse |
| IKT-Kenntnisse | Sehr gute Kenntnisse: IPSEpro, MS Windows, MS Office<br>Grundkenntnisse in: ASPEN PLUS, gPROMS, Matlab, LabView, C/C++ |
| Fremdsprachen (CEFR Stufe) | Englisch (C2), Italienisch (B1), Spanisch (A1-A2) |
| Führerschein | A und B |
| Präsenzdienst | abgeleistet (11/1999 – 06/2000) |
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## Referenzen

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Wien am 21.12.2012

# Publikationsliste

## Begutachtete Zeitschriftenartikel (peer review):

Kravanja P., Modaressi A. und Friedl A. (2012) Heat integration of biochemical ethanol production from straw - A case study**. APPLIED ENERGY** DOI 10.1016/j.apenergy.2012.08.014

Modarresi A., Kravanja P. und Friedl A. (2012) Pinch und exergy analysis of lignocellulosic ethanol, biomethane, heat and power production from straw. **APPLIED THERMAL ENGINEERING** 43:20-28

Kravanja P., Könighofer K., Canella L., Jungmeier G. und Friedl A. (2012) Perspectives for the production of bio-ethanol from Wood und Straw in Austria -Technical, economic and ecological aspects. **CLEAN TECHNOLOGIES UND ENVIRONMENTAL POLICIES** 14:411-425

Kravanja P. und Friedl A. (2011) Process Simulation of Ethanol from Straw – Validation of scenarios for Austria. **CHEMICAL ENGINEERING TRANSACTION** 25:863-868

Lassmann T., Kravanja P. und Friedl A. (2011) Prozess-simulation der Produktion von Ethanol und Methan aus lignocellulosehaltigen Rohstoffen. **CHEMIE INGENIEUR TECHNIK** 83(10):1609-1617

Modarresi A., Kravanja P. und Friedl A. (2011) Exergy analysis of the production of lignocellulosic ethanol. **CHEMICAL ENGINEERING TRANSACTION** 25:635-640

Kravanja P. und Friedl A. (2010) Evaluation of ethanol from lignocellulosic biomass – Process scenarios for Austria. **CHEMICAL ENGINEERING TRANSACTION** 21:1141-1146

## Konferenzvortrag:

Kravanja P.; Könighofer K.; Canella L.; Jungmeier G.; A. Friedl 2nd generation ethanol in Austria - Technical, environmental and economic aspects. **XIX INTERNATIONAL SYMPOSIUM ON ALCOHOL FUELS***,* Verona, Italy 10.10.2011 - 14.10.2011.

## Poster:

Kravanja P., Bösch P. und Friedl A. (2009) Simulation of Ethanol from Lignocellulosic Biomass - Process Options for Austria. **5TH INTERNATIONAL CONFERENCE ON ENVIRONMENTAL ENGINEERING AND MANAGEMENT ICEEM 05**

## Berichte:

Könighofer K., Canella L., Jungmeier G., Kravanja P. und Friedl A. (2012) Bioethanol aus Holz und Stroh – Energieträger- und Technologiebewertung für Bioethanol aus Holz und Stroh. **ENDBERICHT: FFG-PROJEKT NR.: 818921**

Rodrigues D., Kravanja P., Nagy J., Bösch P., Wukovits W. und Friedl A. (2010) Evaluierung eines geeigneten Simulationstool für pyrometallurgische. **PROJEKTENDBERICHT (INTERN).**

## Diplomarbeit (eigene):

Kravanja P. (2008) Cold flow studies in a stationary gas solid fluidized bed. **DIPLOMARBEIT, TU WIEN**

## Diplomarbeiten (mitbetreut):

Weinwurm F. (2010) Heisswasservorbehandlung von Stroh - Eine Methodenentwicklung zur Ausführung und Auswertung im Labormaßstab. **DIPLOMARBEIT, TU WIEN**

Lassmann T. (2012) Downstream processing in ethanol production from lignocellulosic biomass – Process simulation with ASPEN PLUS **DIPLOMARBEIT, TU WIEN**

Castro R. (2012) Process simulation of biogas production from micro- and macroalgae **DIPLOMA THESIS, UNIVERSITY OF BRAGA (PORTUGAL)**