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Jesse Kautto

# EVALUATION OF TWO PULPING-BASED BIOREFINERY CONCEPTS

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# Abstract

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The viability of two biorefinery concepts is evaluated: the extraction of hemicelluloses from wood chips prior to kraft pulping for the production of paper-grade pulp and ethanol, and organosolv pulping for the production of ethanol, lignin and other co-products.

Hemicellulose extraction through prehydrolysis is conventionally applied in the production of dissolving pulp. In this thesis, the prehydrolysis process is studied as a pre-extraction method combined with paper-grade pulp production. The premise of such paper-grade pulp production concept is in more efficient utilization of hemicelluloses: a large share of the hemicelluloses is dissolved in cooking and combusted in the recovery boiler. Water prehydrolysis before cooking would enable extracting them partially and converting them to more value-added products than energy. This was the premise also in the BiSe project (2007 – 2010) in which the thesis work related to hemicellulose extraction was carried out primarily in 2009 – 2010. Two related publications, in which softwood was used as raw material, were published in 2010.

A technical evaluation of the hemicellulose extraction concept was carried out. The evaluation covered the effects of the process on the operation of the pulp mill and pulp quality, and the conversion of the generated prehydrolyzate to ethanol. The evaluation included laboratory experiments carried out in the BiSe project, a simulation model built based on them and an extensive literature review. In the water prehydrolysis and cooking experiments of Scots pine (softwood), the yields on wood after cooking decreased considerably, which, in constant pulp production, resulted in a considerable increase in wood consumption. The increased wood consumption indicated that water prehydrolysis would not lead to more efficient utilization of hemicelluloses.

In addition to increased wood consumption, also other disadvantages were identified. With 14 % of the wood material exctracted, hemicellulose extraction was found to result in a relatively low ethanol output. With a low carbohydrate concentration and problems associated with sticky precipitates and inhibitory compounds, the processing of the prehydrolyzate to ethanol was expected to be difficult and costly. Water prehydrolysis also increased the load on the evaporation plant and recovery boiler considerably, and the effects on the quality of the produced pulp were found to be inconclusive at best. For general paper-grade pulp production, the concept was therefore not considered attractive. While the focus of the study is on the co-production of paper-grade pulp and ethanol, it is reminded in the thesis that prehydrolysis in combination with kraft pulping is common practice in dissolving pulp production. The recovery and use of the sugars present in the prehydrolyzates of dissolving pulp production would be considerably more attractive than the concept studied in this thesis.

Organosolv pulping was originally designed for the production of paper-grade pulp but the process has also been considered as a potential pretreatment and fractionation step in the production of lignocellulosic ethanol or other biofuels or chemicals. As a pretreatment step, the key advantage of organosolv pulping is the ability to recover so-called organosolv lignin, which is a high purity and narrow molecular weight distribution lignin product. In the thesis, a conceptual process design, a simulation model and an economic assessment of an organosolv cooking-based biorefinery were developed based on available literature. In the studied process, hardwood chips are cooked in a mixture of ethanol, water and sulfuric acid (catalyst). Economic feasibility was assessed by the minimum price of ethanol that is required to cover the costs of production and make a certain return on the invested capital (so called Minimum Ethanol Selling Price). The process was compared to a dilute-acid pretreatment-based ethanol production process. The research work was carried out primarily in 2010 – 2011, and the two related articles were published in 2013 and 2014.

With a feed of 2000 dry t/d debarked hardwood chips, the modeled organosolv process produced 459 t/d (53.9 million gallons/204 million liters per year) of ethanol. The process produced also considerable amounts of organosolv lignin and smaller amounts of other co-products, furfural and acetic acid. Due particularly to the recovery of the solvent, the process was found to consume more energy than the reference dilute acid process. This, along with the recovery of co-products, resulted in a need of external fuel to cover the steam demand. With a more complex flowsheet, the organosolv process was also found to have a higher investment cost than the reference process. The economic assessment showed that the price of organosolv lignin largely dictates whether the key advantage, the recovery of the lignin, outweighs the two main disadvantages, higher energy consumption and capital costs. With a base case lignin price of 450 USD/t, the minimum ethanol selling price of the organosolv process was higher than that of the reference process. A higher lignin price was required to make the organosolv process cost-competitive, demonstrating the importance of finding higher-valued applications for the lignin. As a conclusion, it can be stated that the organosolv concept can be generally considered as attractive if higher-priced applications for the organosolv lignin can be identified. Data from larger-scale experiments, as well as application testing and market development work related to organosolv lignin would, however, be needed to improve the accuracy of the evaluation of the concept.

Keywords: Hemicellulose extraction, prehydrolysis, organosolv, pulping, biorefinery, bioethanol

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This doctoral thesis is the result of a long journey. Many people have contributed to the completion of it and deserve to be acknowledged. I started my doctoral research in the summer of 2009 in the Technology Business Research Center of Lappeenranta University of Technology (LUT). I then worked as a visiting researcher in Georgia Institute of Technology, Institute of Paper Science and Technology from July 2010 to September 2011. After these little over two years, I started to work outside the academia, at Pöyry Management Consulting Oy, and finalized the thesis on my own time in 2011 – 2017. First and foremost, I would wish to acknowledge my supervisor, Professor Tuomo Kässi who patiently supported me throughout the project and let me carry out the work in my own way. In the beginning of the project, I also received considerable support from Professor Kaj Henricson. I thank him for the very valuable professional advice and the numerous interesting discussions we had. In Georgia Institute of Technology, my primary supervisor was Professor Matthew J. Realff. In Dr Realff's guidance, I took a notable step forward in the modeling and evaluation of different biomass conversion processes. These learnings, for which Dr Realff is greatly acknowledged, are well visible on the pages of this thesis. I also would like to thank Professor Arthur Ragauskas warmly for his support and for making my visit in Georgia Institute of Technology possible. I thank the pre-examiners of the thesis, Professor Adriaan van Heiningen and Docent Markku Karlsson, whose insightful comments helped to improve the quality of the thesis considerably.

The thesis project was started in a research project called BioRefinery pulp mill (BiSe). The project was financed by TEKES (the Finnish Funding Agency for Technology and Innovation) and project member companies (Andritz Oy, Finex Oy, Honeywell Oy, Stora Enso Oyj, Sunila Oy (merged into Stora Enso Oyj during the project) and UPM-Kymmene Oyj). The member companies are greatly acknowledged for the committed resources, participation and guidance during the BiSe project. Also all the researchers in the project partner universities, LUT, the University of Jyväskylä and Helsinki University of Technology (currently Aalto University) are acknowledged. Particular thanks are given to Dr Esa Saukkonen, for all the cooperation, Tiina Nokkanen, who was the primary organizer of the project and the laboratory experiments carried out in it, and Professor Raimo Alén, for the support in this thesis project. In addition to the BiSe project, I received funding from The Finnish Cultural Foundation, Walter Ahlström Foundation and Tekniikan edistämissäätiö. All these foundations are greatly acknowledged for funding this research.

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Jesse Joonas Kautto
August 2017
Helsinki, Finland

# Contents

**Abstract**

**Acknowledgements**

**Contents**

**List of publications** **9**

**List of figures** **11**

**List of tables** **12**

**List of symbols and abbreviations** **13**

**1 Introduction** **17**
- 1.1 Background and motivation ... 17
- 1.2 Positioning of the study ... 21
- 1.3 Research objectives ... 24
- 1.4 Limitations of the scope of the study ... 27
- 1.5 Outline of the thesis ... 28

**2 Lignocellulosic biorefinery concepts** **31**
- 2.1 Biochemical processes ... 32
  - 2.1.1 Pretreatment ... 32
  - 2.1.2 Hydrolysis ... 38
  - 2.1.3 Fermentation and product recovery ... 39
  - 2.1.4 Techno-economic assessments of lignocellulosic ethanol ... 39
- 2.2 Thermochemical processes ... 42
- 2.3 Pulp mill biorefinery concepts ... 43
  - 2.3.1 Brief description of kraft pulping ... 43
  - 2.3.2 Biorefinery processes integrated to a pulp mill ... 44

**3 Overview of the studied biorefinery concepts** **47**
- 3.1 Hemicellulose extraction prior to kraft pulping ... 47
  - 3.1.1 Background and introduction ... 47
  - 3.1.2 Effects of hemicellulose extraction on pulp mill operation and pulp quality ... 48
  - 3.1.3 Composition of the hemicellulose containining stream and its processing to ethanol ... 60
  - 3.1.4 Techno-economic analyses of hemicellulose extraction combined with pulp production ... 63
- 3.2 Organosolv pulping ... 64
  - 3.2.1 Background and introduction ... 64
  - 3.2.2 Solvent systems and process concepts ... 65

3.2.3 Utilization of fractionated product streams ..... 68
3.2.4 Simulation and techno-economic analyses of organosolv concepts ..... 69

4 Research design 75
4.1 Philosophy of science ..... 75
4.2 Research strategy ..... 75
4.3 Research methodology ..... 77
4.4 Methodological positioning of the study ..... 78
4.5 Specific methods applied within the studied two process concepts ..... 79
4.5.1 Hemicellulose extraction before kraft pulping (Publications I and II) ..... 80
4.5.2 Organosolv pulping (Publications III and IV) ..... 84
4.5.3 Summary and critical review of the methods utilized in Publications I – IV ..... 93

5 Review of the publications and research findings 97
5.1 Publication I: Effects of integrating a bioethanol production process to a kraft pulp mill ..... 97
5.2 Publication II: Digestibility and paper-making properties of prehydrolyzed softwood chips ..... 99
5.3 Publication III: Design and simulation of an organosolv process for bioethanol production ..... 102
5.4 Publication IV: Economic analysis of an organosolv process for bioethanol production ..... 105
5.5 Summary of the publications ..... 110
5.6 Research findings ..... 112
5.6.1 Hemicellulose extraction (research questions Q1 – Q2) ..... 112
5.6.2 Organosolv process (research questions Q3 – Q5) ..... 115

6 Discussion 119
6.1 Revisit to Publication I, load increases in the evaporation plant and recovery boiler ..... 119
6.2 Summary of the findings and the main research question ..... 120
6.2.1 Conceptual feasibility of hemicellulose pre-extraction prior to kraft pulping ..... 121
6.2.2 Conceptual feasibility of organosolv pulping ..... 125
6.3 Theoretical contribution ..... 128
6.4 Practical implications ..... 129
6.5 Limitations of the research findings ..... 131
6.6 Suggestions for further research ..... 133

7 Conclusions 135

References 137

Publications

# List of publications

This thesis is based on the following publications. The rights to include these publications in the thesis have been granted by the publishers. For Publication 1, the rights were granted only for the printed version of the thesis. The publication is therefore not included in the electronic version.

### Publication I

Kautto, J., Henricson, K., Sixta, H., Trogen, M. and Alén, R. (2010a). Effects of integrating a bioethanol production process to a kraft pulp mill. *Nordic Pulp and Paper Research Journal*, 25(2), pp. 233-242.

### Publication II

Kautto, J., Saukkonen, E. and Henricson, K. (2010b). Digestibility and paper-making properties of prehydrolyzed softwood chips. *BioResources*, 5(4), pp. 2502-2519.

### Publication III

Kautto, J., Realff, M.J. and Ragauskas, A.J. (2013). Design and simulation of an organosolv process for bioethanol production. *Biomass Conversion and Biorefinery*, 3(3), pp. 199-212.

### Publication IV

Kautto, J., Realff, M.J., Ragauskas, A.J. and Kässi, T. (2014). Economic analysis of an organosolv process for bioethanol production. *BioResources*, 9(4), pp. 6041-6072.

# Author's contribution

### Publication I

Analyzing the experimental data produced in the BiSe project and developing the simulation model. Interpreting the results of the simulation model and writing the manuscript.

### Publication II

Responsible author in the cooking and oxygen delignification sections of the publication. Analyzing and interpreting the experimental data produced in the BiSe project and writing the manuscript together with Dr Esa Saukkonen.

**Publication III**

Collecting and analyzing literature data and developing the conceptual process design and simulation model. Interpreting the results of the simulation model and writing the manuscript.

**Publication IV**

Carrying out the economic calculations, interpreting the results and writing the manuscript.

## Supporting publications

Saukkonen, E., Kautto, J., Rauvanto, I. and Backfolk, K. (2012b). Characteristics of prehydrolysis-kraft pulp fibers from Scots pine. *Holzforschung,* 66(7), pp. 801-808.

Hamaguchi, M., Kautto, J. and Vakkilainen, E. (2013). Effects of hemicellulose extraction on the kraft pulp mill operation and energy use: review and case study with lignin removal. *Chemical Engineering Research and Design*, 91(7), pp. 1284-1291.

# List of figures

Figure 1: Focus area of the research. ........ 22
Figure 2: Steps in chemical product and process design. ........ 24
Figure 3: Outline of the thesis. ........ 29
Figure 4: Overview of biochemical and thermochemical biorefinery concepts. ........ 32
Figure 5: Block diagram of a conventional pulp mill and additional process steps. ........ 45
Figure 6: Schematic representation of a Lignol-type ethanol-based organosolv pulping process. ........ 68
Figure 7: Methodological positioning of the thesis. ........ 79
Figure 8: Schematic dry solids mass balance over organosolv cooking, post-hydrolysis and lignin separation assumed in the model. ........ 87
Figure 9: The main working methods applied in the thesis. ........ 94
Figure 10: Block diagram of the modeled ethanol organosolv biorefinery. ........ 103
Figure 11: The effect of the selling price of lignin on the MESP of the organosolv process. . ........ 109
Figure 12: Studied hemicellulose extraction -based pulp and ethanol -producing biorefinery. ........ 113
Figure 13: Tentative dry solids mass balances over a hemicellulose extraction –based pulp and ethanol -producing biorefinery and a conventional pulp mill. ........ 114

# List of tables

Table 1: Conditions applied in pretreatment and the effects of pretreatment on a poplar feedstock. ........ 36
Table 2: Xylose and glucose yields in pretreatment (denoted as Stage 1) and enzymatic hydrolysis (Stage 2). ........ 37
Table 3: Techno-economic assessments of lignocellulosic ethanol. ........ 41
Table 4: Review of a selected list of recent hemicellulose extraction studies. ........ 49
Table 5: Summary of the effects of water prehydrolysis on fiberline, chemical recovery and pulp quality. ........ 59
Table 6: Review of simulation studies evaluating the simultaneous production of paper-grade pulp and ethanol based on hemicellulose extraction. ........ 62
Table 7: Process design and simulation studies on organosolv processes. ........ 70
Table 8: Techno-economic studies on organosolv processes. ........ 72
Table 9: Chemical composition of the prehydrolyzate (as weight-% of original wood dry solids) from water prehydrolysis of pine wood chips at different P-factors. ........ 80
Table 10: Cooking and oxygen delignification of prehydrolyzed and reference chips. ........ 82
Table 11: Conditions and chemical charges in oxygen delignification and bleaching .. 84
Table 12: Process areas and bases of costing. ........ 91
Table 13: Schedule and cash flow in plant planning and engineering, construction and start-up. ........ 92
Table 14: Summary of the main findings of Publication II. ........ 101
Table 15: The raw materials and products of the process. ........ 104
Table 16: Investment cost analysis. ........ 106
Table 17: Breakdown of the MESP of the organosolv process to cost contributors. ... 107
Table 18: Sensitivity of MESP to technical parameters, investment cost and discount rate ........ 108
Table 19: A summary of the publications in the thesis. ........ 111
Table 20: Key advantages and disadvantages of hemicellulose extraction through water prehydrolysis prior to kraft pulping for the production of ethanol. ...... 122
Table 21: Key technical advantages and disadvantages of organosolv pulping for the production of ethanol (as compared to dilute acid pretreatment –based ethanol production). ........ 126

# List of symbols and abbreviations

**Latin alphabet**

| | |
|---|---|
| β-O-4 | β-O-4 aryl ether lignin linkage |
| a | Year |
| Acetosolv | Acetic acid-water (with HCl as a catalyst) pulping process |
| Adt | Air dry ton |
| AFEX | Ammonia fiber explosion |
| ALCELL | Ethanol-water pulping process |
| ASAM | Alkali-sulfite-anthraquinone-methanol pulping process |
| ARP | Ammonia recycle percolation |
| C5 | Five-carbon sugar, pentose |
| C6 | Six-carbon sugar, hexose |
| CBP | Consolidated bioprocessing |
| CI | Crystallinity index |
| CSF | Canadian standard freeness |
| d | Day |
| DED | Chlorine dioxide – alkaline extraction – chlorine dioxide bleaching sequence |
| DOP | Degree of polymerization |
| EA | Effective alkali |
| EUR | Euro |
| gal | Gallon |
| h | Hour |
| H-factor | Single variable expression of pulping time and temperature |

| | |
|---|---|
| IFBR | Integrated forest biorefinery |
| IRR | Internal rate of return |
| ISO | International Standards Organisation |
| kt | Kiloton (1000 tons) |
| L | Liter |
| LCC | Lignin carbohydrate complexes |
| LMW | Lower molecular weight |
| LTW | Liquor-to-wood ratio |
| mboe | Million barrels of oil equivalent |
| MESP | Minimum ethanol selling price |
| MEUR | Million Euro |
| MILOX | Formic acid-performic acid pulping |
| min | Minute |
| NPV | Net present value |
| NREL | National Renewable Energy Laboratory |
| O | Oxygen delignification |
| Odt | Oven dry ton |
| Organocell | One- or two-stage alkaline pulping process using mainly methanol, water and NaOH |
| P-factor | Prehydrolysis factor, single variable expression of prehydrolysis time and temperature |
| PFI | Paper and Fibre Research Institute |
| RED | Renewable Energy Directive |
| SPORL | Sulfite pretreatment to overcome lignocelluloses recalcitrance |
| SSF | Simultaneous saccharification and fermentation |

| | |
|---|---|
| t | (metric) Ton |
| TTA | Total titratable alkali |
| USD | United States dollar |
| VPP | Value prior to pulping |
| vol-% | Volume percentage |
| wt-% | Weight percentage |

# 1 Introduction

## 1.1 Background and motivation

The non-renewability of fossil fuels and their contribution to carbon dioxide emissions have generated interest in, and demand for biofuels. The demand for transportation biofuels has further been intensified by policy instruments promoting their use. Biofuels are currently produced globally on a relatively large scale. In 2011, 1.3 million barrels of oil equivalent per day (mboe/d) were produced, representing 3 % of the global road transport energy use (IEA 2013). The largest biofuel market is currently the US, followed by Brazil and the European Union (IEA 2013). The dominant biofuel is ethanol (global total 1.0 mboe/d in 2011), which is produced almost exclusively from edible parts of plants, including particularly corn starch in the US and sugar cane sugar in Brazil (IEA 2013), and it thus belongs to the category of so-called first generation or conventional biofuels.

With concerns over their sustainability, the use of food crops for the production of biofuels has recently been a topic of debate. The sustainability issues associated with first generation biofuels include concerns over the effect of biofuel feedstock on deforestation and the land used to grow food (IEA, 2013). Second generation or advanced biofuels, using non-food feedstocks as raw material, have been seen as a way to reduce or eliminate the concerns related to biofuel production (IEA 2013). As suitable non-food feedstock for biofuel production, especially various lignocellulosic biomass fractions have been considered. These include agricultural residues such as corn stover, straws and sugarcane bagasse, forest biomass and woody residues (hardwoods and softwoods, various forest residues, as well as mill residues from the forest industry), and herbaceous grasses such as switchgrass (see e.g. Huang et al. 2009; U.S. Department of Energy 2011). Policy instruments have been put in place to promote the production of second generation biofuels in the US (specific blending quota for cellulosic biofuels) and the EU (biofuels produced from waste and cellulosic feedstocks are double-counted in the 10 % renewable energy target for transport by 2020) (IEA 2014). Beyond 2020, the European Commission’s updated proposal of the Renewable Energy Directive (RED) (often referred to as REDII) outlines a maximum contribution of 3.8 % from liquid biofuels produced from food and feed crops towards the renewable energy targets by 2030. Furthermore, fuel suppliers have an obligation to supply at least 3.6 % of advanced biofuels produced from the lignocellulosic, waste-based and other raw materials listed in Annex IX of the proposal (European Commission 2017).

Lignocellulosic raw materials are generally more complex than first generation feedstocks and require therefore more processing steps in biofuel production. The lignocellulosic biomass needs to undergo pretreatment or fractionation steps before the actual conversion to a biofuel. In addition to biofuels, the fractionated streams can be converted to biochemicals and various biomaterials. With the various fractionation and conversion steps, these production technologies have been seen as analogous to oil refineries and are often termed as *biorefineries*. Several technological routes from lignocellulosic biomass to biofuels exist. These routes are generally grouped into *thermochemical* and *biochemical* ones. In thermochemical routes, biomass is treated thermally into a state which enables its conversion into biofuels. Such routes include particularly various gasification and pyrolysis technologies. In biochemical routes in turn, biomass is converted to a form that can then be fermented by microorganisms (such as bacteria and yeast) to biofuels. As the biochemical routes are typically based on the fermentation of sugars that can be liberated from the biomass, they are therefore often termed also as the *sugar platform* (NREL 2009). This study focuses on the biochemical route. Although many of the findings of the study are applicable to several different biofuels and biochemicals produced through the biochemical route, the specific focus is on the production of lignocellulosic ethanol.

Lignocellulosic ethanol has been a point of interest in recent years both academically and commercially. The first larger demo and commercial scale lignocellulosic ethanol facilities, e.g. the Beta Renewables' plant in Crescentino, Italy (Biofuels Digest 2013) and POET-DSM' plant in Emmetsburg, Iowa (Biofuels Digest 2014), have been built already. The production of lignocellulosic ethanol through the biochemical route consists typically of the following four major steps: pretreatment, hydrolysis, fermentation, and purification of the ethanol product stream. Pretreatment is needed to overcome the natural recalcitrance of the lignocellulosic plant biomass towards enzymatic hydrolysis, due to the chemical and structural composition of the plant biomass (Himmel et al. 2007). In pretreatment, the material undergoes mechanical, physical, chemical and/or biological treatment for the disruption of its cell wall structure, making it more amenable either to enzymatic or chemical hydrolysis treatment. Enzymatic hydrolysis is the more typical hydrolysis method, and the primary effects of the pretreatment include the removal of lignin carbohydrate complexes (LCC) and modification and redistribution of lignin (Chundawat et al. 2011), as well as solubilization of hemicelluloses and reduction in the crystallinity of cellulose, thereby facilitating the subsequent enzymatic hydrolysis of the cellulose (Mosier et al. 2005; Zheng et al. 2009; Chundawat et al. 2011). After pretreatment, the carbohydrates present in the biomass are converted to monomeric sugars in the abovementioned hydrolysis step, and the sugars are fermented to ethanol.

Several pretreatment or fractionation methods have been suggested in the literature, including uncatalyzed and acid catalyzed steam explosion, liquid hot water, dilute acid, alkaline, ammonia fiber explosion (AFEX), and organosolv (Hamelinck et al. 2005; Mosier et al. 2005; Kumar et al. 2009). The pretreatment step has generally been estimated to be one of the most expensive capital investments in a lignocellulosic ethanol plant (see e.g. Kazi et al. 2010). As it furthermore has a considerable effect on the functioning of enzymatic hydrolysis and fermentation (Tao et al. 2011), the development and selection of the pretreatment method could have a decisive effect on the economic feasibility of lignocellulosic ethanol. Although the first larger lignocellulosic ethanol plants appear to rely on steam explosion or a similar technology based on pressurized vessels and rapid decompression (POET-DSM 2012; Beta Renewables 2014), evaluation and comparison of different pretreatment methods is ongoing in the academic literature.

Recent literature includes both experimental studies evaluating the characteristics of different pretreatment steps and their effect on the downstream operation, as well as broader simulation and techno-economic studies deriving their key parameters from experimental work (see e.g. Tao et al. 2011; Kumar and Murthy 2011; Uppugundla et al. 2014).

In addition to the actual pretreatment and fractionation technologies and the downstream production of lignocellulosic ethanol, several other aspects, such as the cost of feedstock and the enzyme cost have an effect on the economics of the process (Kazi et al. 2011). Also, aspects related to the possible integration of the bioethanol production process to an existing industrial facility have been discussed in the literature. Various integration schemes have been suggested, including the integration of second generation ethanol production to existing first generation sugarcane or corn ethanol plants. For example, the integrated processing of sugarcane juice (first generation feedstock) and sugarcane bagasse and trash (second generation feedstock) to ethanol could lead to improvements in biomass logistics, integrated use of parts of the infrastructure and equipment, as well as reduced level of inhibition in fermentation (assuming that the first and second generation sugars would be fermented in the same tanks) (Dias et al. 2012). Another possible platform for integration is existing forest industry facilities, and particularly existing pulp mills. Similarly to integration to an existing ethanol plant, benefits could be found in biomass logistics and integrated use of plant infrastructure. Diversifying the production of existing forest industry facilities to include biofuels and other novel bio-based materials has furthermore been seen as a possible approach to improve the economic situation of forest industry companies. Pulp mill -based biorefineries, co-producing pulp and novel bio-based products such as fuels and chemicals, have been called integrated forest biorefineries (IFBR) (van Heiningen 2006). Various options to convert a traditional pulp mill into an IFBR could include the extraction of hemicelluloses from wood chips prior to pulp cooking, separation of lignin from black liquor, as well as black liquor gasification (van Heiningen 2006). The hemicelluloses extracted from wood chips could be converted to monomeric sugars and fermented to ethanol, enabling the co-production of pulp and ethanol (van Heiningen 2006; Frederick et al. 2008). The separated lignin, as well as the synthesis gas produced from black liquor could also be converted to various novel bio-based products. An IFBR, separating and converting one or several pulp mill streams to novel products, is essentially a multi-product biorefinery.

Drawing from the context of pulp mill-based biorefinery concepts, a research project called Biorefinery pulp mill (BiSe) was undertaken in 2007 – 2010. The project was financed by TEKES (the Finnish Funding Agency for Technology and Innovation) and project member companies (Andritz Oy, Finex Oy, Honeywell Oy, Stora Enso Oyj, Sunila Oy (merged into Stora Enso Oyj during the project) and UPM-Kymmene Oyj). The project research partners were Lappeenranta University of Technology, University of Jyväskylä and Helsinki University of Technology (currently Aalto University). A specific focus in the project was on the extraction of hemicelluloses from wood chips prior to cooking through a so-called prehydrolysis process. Combined with kraft cooking, the prehydrolysis process is conventionally used in the production of dissolving pulp. The focus in the BiSe project was, however, on the production of paper-grade pulp. In retrospect, this decision could perhaps be attributed to two primary, time-specific factors. The first relates to research trends taking place at the time the project was developed and initiated. As indicated above, the extraction of hemicelluloses for the co-production of paper-grade pulp and co-products, such as ethanol, was widely studied in the academic world in the second half of the 2000s. The premise of this co-production concept was in more efficient utilization of hemicelluloses. Since a large share of the hemicelluloses is dissolved in cooking and combusted in the recovery boiler, it was thought that water prehydrolysis before cooking would enable extracting them partially and converting them to more value-added products than energy. This premise was the starting point in the BiSe project. In the second half of the 2000s, the Finnish forest industry was furthermore faced with rapid restructuring, resulting in the closing of several pulp and paper mills. The extraction of hemicelluloses and the generation of e.g. ethanol were seen in the BiSe project as a way to develop new revenue streams and improve the competitive position of Finnish pulp mills. While particularly the pulp industry has witnessed a strong revival in the 2010s, the economic uncertainties of the previous decade were the background for the start of the BiSe project.

Another fractionation concept that has its background in the pulping industry and enables the production of multiple products is organosolv pulping (Aziz and Sarkanen 1989; Hergert 1998; Pan et al. 2005; Pan et al. 2006). In organosolv pulping, lignocellulosic biomass is fractionated with the aid of organic solvents and high temperature into a solid pulp fraction rich in cellulose, an aqueous stream rich in hemicellulosic sugars and a relatively pure lignin product. As the produced pulp is suitable for paper manufacture, organosolv pulping was originally designed for the production of paper-grade pulp. The produced pulp has, however, been found to have a very good response to enzymatic hydrolysis, making organosolv pulping a potential pretreatment and fractionation method in the production of lignocellulosic ethanol. In addition to lignin, organosolv pulping enables the recovery of acetic acid and furfural.

The feasibility of two biorefinery concepts are evaluated in this study: the extraction of hemicelluloses from wood chips prior to kraft pulping for the production of paper-grade pulp and ethanol and organosolv pulping for the production of ethanol, lignin and other co-products (for the block diagrams of the studied concepts, see Figure 12 in subchapter 5.6.1 (hemicellulose extraction) and Figure 10 in subchapter 5.3 (organosolv pulping)). The studied organosolv pulping concept uses ethanol as the solvent. Concerning hemicellulose extraction, the work leading to the results presented in this thesis was carried out predominately within the framework of the BiSe project, primarily in 2009 – 2010. Two publications included in the thesis (Publications I and II) were published in 2010. The work related to organosolv pulping was in turn carried out primarily by the author as a visiting researcher in Georgia Institute of Technology, Atlanta, USA, between summer 2010 and autumn 2011. The publications related to the research (Publications III and IV) were published in 2013 and 2014. The long time period between the start of the doctoral thesis (2009) and the finalization of the thesis (2017) is due to the fact that author has been working outside the academia since the autumn of 2011.

Regarding the hemicellulose extraction concept, a relatively small amount of the wood material can be extracted prior to kraft pulping. The main product is therefore the pulp, and the feasibility of the hemicellulose extraction concept depends to a considerable degree on the effects of the extraction on the quality of the pulp and the operation of the pulp mill. The hemicellulose extraction concept is evaluated in this thesis predominately from these perspectives. Although there exists a large body of literature on hemicellulose extraction and subsequent pulping, relatively few studies have covered the technical aspects of the whole pulp mill, from extraction, pulping and bleaching to chemical recovery and the quality of the produced pulp. Covering all these aspects has enabled a comprehensive evaluation of the feasibility of the concept.

The organosolv biorefinery concept was in turn assumed to be a stand-alone green field plant. Based on a detailed simulation model, both the technical and economic feasibility of the plant was evaluated. Although various pretreatment and fractionation technologies have been evaluated in the literature, similar comprehensive analyses of the feasibility of the ethanol-based organosolv process for the production of bioethanol and co-products had not been presented previously.

## 1.2 Positioning of the study

It has been argued that with the finite nature of fossil raw materials and the contribution of their use on global warming and other environmental issues, an increasing share of fuels and chemicals would need to be produced from renewable, bio-based raw materials (Thoen and Busch 2006). Further drivers for the transition to a bio-based economy could include the diversification of energy sources and the dependency of many countries on fossil fuel imports, as well as the stimulation of regional and rural development (de Jong et al. 2012). In the production of bio-based fuels and chemicals, much emphasis has been put on the development and emergence of *biorefineries*. Various definitions exist for biorefineries. The National Renewable Energy Laboratory (NREL) in the US defines biorefinery as “a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry.” (NREL 2009). As the most abundant types of biomass raw materials globally are lignocellulosic raw materials, *lignocellulosic biorefineries* (for a classification of different biorefinery concepts see e.g. Kamm and Kamm (2004)), the processing of lignocellulosic biomass to fuels, chemicals, and materials has been of specific interest recently. Numerous lignocellulosic biorefinery concepts have been presented, with differing raw materials, conversion technologies and end-products (see Chapter 2). As examples of novel lignocellulosic biorefineries, the first larger lignocellulosic ethanol plants have recently started their operation (see subchapter 1.1). In principle, a conventional pulp mill, producing pulp, electricity and tall oil, could also be considered a lignocellulosic biorefinery.

With biorefineries and the processing of biomass to bio-based fuels, chemicals and materials forming the context and background of the thesis, the focus of the thesis is on the intersection of three broad fields, chemical engineering, pulp and paper technology and industrial engineering and management (Figure 1). Two specific types of lignocellulosic biorefinery concepts are studied from the perspective of their overall feasibility: hemicellulose extraction prior to kraft pulping for the co-production of ethanol and pulp, and organosolv pulping for the production of ethanol.

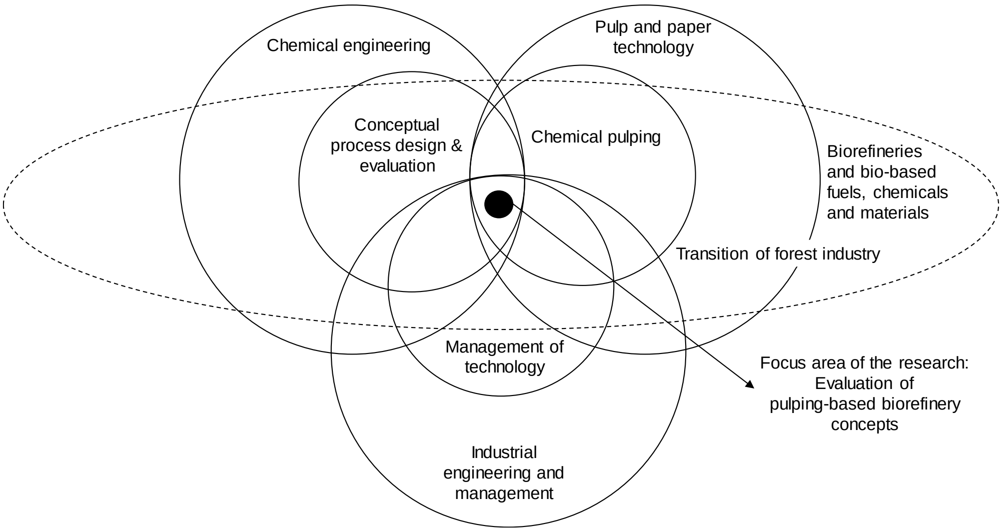


Figure 1: Focus area of the research.

In the field of pulp and paper technology, the focus is specifically on chemical pulping. Chemical pulping can be defined as a process where the lignin present in plant material is softened and dissolved by the aid of chemical reactants and heat (see subchapter 2.3.1). The basis for both of the studied biorefinery concepts is the chemical pulping process. However, the two studied biorefinery concepts utilize different cooking chemicals and apply the pulping technology itself to produce a different type of a product. In the first concept, hemicellulose extraction, hemicelluloses are extracted prior to a conventional pulping process called the kraft pulping process, enabling the co-production of paper-grade pulp and ethanol. While the background of the second chemical pulping process, called organosolv pulping, is also in the production of paper-grade pulp, it has recently been studied as a pretreatment step prior to enzymatic hydrolysis of lignocellulosic material to sugars, enabling its further conversion to ethanol (see subchapter 3.2.1). As the first studied biorefinery concept aims at producing paper-grade pulp, a key aspect in the feasibility of the concept is the quality of the pulp. In the evaluation of the quality of the produced pulp, the focus of the thesis is partially also on paper technology.

In the field of chemical engineering, the work carried out in this thesis relates particularly to process design. The lifecycle of process design can be considered to consist of various steps, from early stage synthesis and screening of process concepts to more detailed design work, followed finally by construction, startup and production (see e.g. Seider et al. 2009). In the process design procedure presented by Seider et al. (2009), which follows closely Cooper's Stage-Gate model (Cooper 2001), the present work could be considered to be located especially in the concept stage. Some of the activities characteristic to the stage carried out in this thesis work include opportunity assessment (typically including cost estimates, risks, and, especially for basic chemical products, the profitability of the manufacturing process), database creation (typically including thermophysical and price data), and preliminary process synthesis (typically including the main reaction, separation and temperature, and pressure change operations). In addition, experimental laboratory work is often carried out in the concept stage (Seider et al. 2009). Although experimental work was not carried out by the author of this thesis, collection, analysis and interpretation of experimental data both from the BiSe research project, as well as from the literature were carried out throughout this thesis. Experimental data was furthermore utilized in the conceptual process designs developed in the thesis.

Some of the characteristics of the next, the feasibility stage, can also be found in this thesis, including the development of base case designs (typically including a flow diagram, material and energy balances and a list of the main equipment, which are often compiled with the aid of computer-aided process simulator software) and the use of algorithmic methods (including synthesis of separation trains). Although the thesis work included some aspects of this more detailed feasibility stage, the work carried out was entirely *conceptual*. It did not include for example data from pilot scale runs to validate the assumptions adopted in the simulation models and discussions with equipment suppliers were limited to a number of key process units. No comprehensive discussions with equipment suppliers on the specifications of the equipment and their costing were carried out in this study. As presented in Figure 2, the work carried out in this thesis is therefore generally located in the early stages of process design, conceptual process design and evaluation. In addition to positioning the thesis within the lifecycle of a process design project, it can also be positioned within the field of process design based on its context and background. The two biorefinery concepts studied in the thesis include several categories of conversion steps of lignocellulosic biorefineries, including pretreatment, chemical pulping, enzymatic hydrolysis, and isolation of lignin (Kamm et al. 2006), following therefore the general design principles of biorefineries.

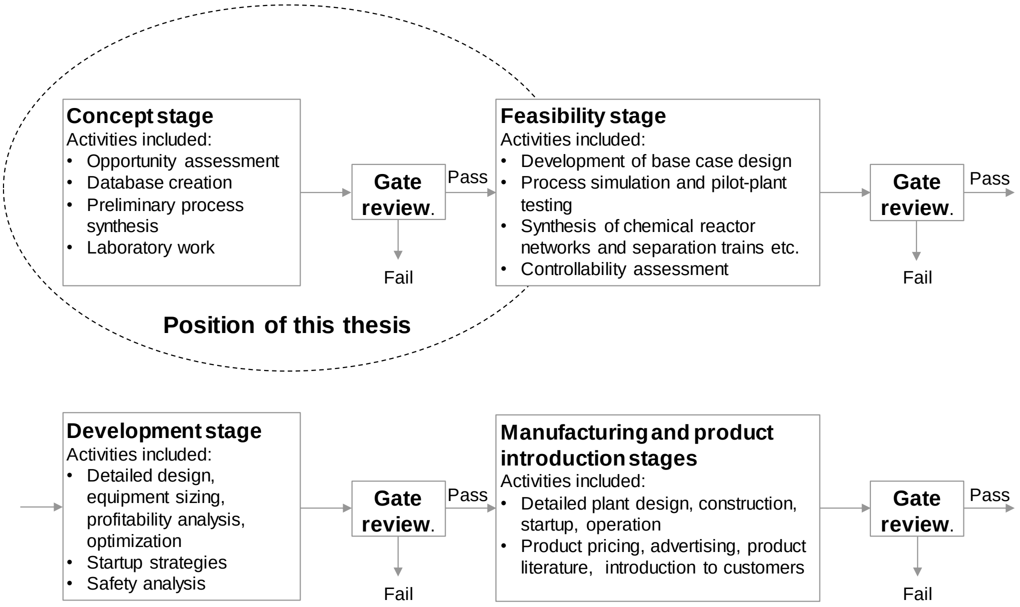


Figure 2: Steps in chemical product and process design (adapted from Seider et al. 2009).

In the field of industrial engineering and management, the work carried out in this thesis relates specifically to the management of technology: to which products, processes, and technologies companies should allocate resources to. The Stage-Gate process presented above in the context of process design (Figure 2) is one tool to manage product development, as well as research and development portfolios (Cooper 2001). The Stage-Gate process systemizes the project evaluation procedure with review gates between different development stages. Various criteria can be used to evaluate the attractiveness of a project at the gates, including technical feasibility, strategic variables such as fit with company objectives and competitive advantage, market attractiveness, and financial metrics such as net present value or internal rate of return (Cooper 2001). Various portfolio management methods can be used to carry out the gate review (Cooper 2001). As this work is not company-specific, the two studied biorefinery concepts are studied purely from technical (both concepts) and economic (organosolv pulping) perspectives, not taking any company-specific aspects into account. As there are multiple biorefinery configurations, the assessments carried out in this work can provide input to the initial screening stages of a project evaluating different process alternatives.

## 1.3 Research objectives

The objective of this thesis is to evaluate the conceptual feasibility of two biomass fractionation methods for the production of lignocellulosic ethanol and other products: pre-extraction of hemicelluloses prior to kraft pulping, and organosolv pulping. The hemicellulose extraction is carried out through a so called prehydrolysis process. In the process, the hemicelluloses present in wood are hydrolyzed and solubilized. If the process is carried out in the aqueous phase, the resulting liquid containing the hemicellulose-based carbohydrates (called prehydrolyzate) can be separated from the wood chips. As mentioned in subchapter 1.1, the prehydrolysis process is conventionally used in the production of dissolving pulp. The studied pre-extraction concept aims, however, at co-production of paper-grade pulp and ethanol or other hemicellulose-based chemicals, fuels or biomaterials. In other words, the study does not consider the production of dissolving pulp from the prehydrolyzed chips. The feasibility of the concept will be evaluated from the technical perspective, evaluating the effects of the hemicellulose extraction concept on the operation of the overall pulp mill and quality of the produced pulp.

The studied organosolv concept aims at fractionating lignocellulosic biomass to three main streams: cellulose, hemicellulosic sugar and lignin -containing streams. Both cellulose and hemicellulose sugars are assumed to be fermented to ethanol. In other words, no other end-uses for these two fractions are assumed in this study. The effect of the recovery of other co-products, namely lignin, furfural and acetic acid, is taken into account in the analysis, however. Both technical and economic aspects are covered in the feasibility analysis.

The main research question is: *Are the two studied processes (pre-extraction of hemicelluloses prior to kraft pulping and organosolv pulping) feasible biomass fractionation and biorefinery concepts?*

To evaluate the conceptual feasibility of the two biorefinery concepts, the following sub-questions were formulated and subsequently addressed during the course of this thesis work:

*Q1: What is the overall process concept for hemicellulose extraction-based ethanol production and what are the mass balances over hemicellulose extraction and cooking, as well as ethanol production?*

The first sub-question was formulated to gain understanding on the amount of ethanol that can be produced from the hemicellulose-containing prehydrolyzate and on the processing steps required to convert the extracted hemicelluloses to ethanol. The analysis was based on experimental analysis of the composition and amount of prehydrolyzate that can be separated from wood chips prior to kraft pulping as well as on simulation work.

*Q2: What is the effect of hemicellulose extraction on the pulp mill fiberline, chemical recovery and the quality of the produced pulp?*

The second sub-question was compiled to elucidate the effect of hemicellulose extraction on the operation of a pulp mill and the quality of the produced pulp. As the main product of a pulp and ethanol -producing biorefinery concept would be the pulp, the feasibility of the concept would be to a considerable degree dictated by these effects. The analysis was based on both experimental and simulation work.

*Q3: What is the overall process concept for an organosolv pulping -based biorefinery, including pulping, ethanol production and the recovery of by-products? How can the process be compared systematically to the more standard dilute acid pretreatment -based lignocellulosic ethanol production?*

The third research question related firstly to the conceptual process design and technical analysis of the organosolv pulping -based biorefinery system. Comprehensive studies on organosolv biorefinery systems, covering the whole process from organosolv pulping to the recovery of ethanol and co-products, had not been presented in the literature previously. The development of the comprehensive flowsheets and simulation model enabled compiling mass and energy balances (research question *Q4*).

The third research question related secondly to the comparison between the organosolv and dilute acid pretreatment -based ethanol production processes. As the dilute acid process can be considered to be a typical pretreatment process that is both more widely studied and better documented than the organosolv process, a systematic approach was developed to compare the two processes. A detailed literature description of the dilute acid process was used both as a reference point, and, whenever applicable, as a design basis for the organosolv process. This enabled systematic comparison of the two processes, providing better understanding of the feasibility of the organosolv process.

*Q4: What are the mass and energy balances of the organosolv process and how does the process compare technically to the dilute acid process?*

Mass and energy balances were compiled based on the developed conceptual process design and simulation model (research question *Q3*). As the dilute acid process was used as a reference point and design basis whenever applicable, the conceptual process design and mass and energy balances enabled comparing the organosolv process to the reference dilute acid process in terms of e.g. ethanol yield and energy consumption. The conceptual process design and balances served also as a sound basis for the economic assessment of the process (research question *Q5*).

*Q5: What is the economic feasibility of the organosolv process for bioethanol production? How does it compare economically to the dilute acid pretreatment -based ethanol production process?*

From the technical perspective (research questions *Q3* and *Q4*), the organosolv biorefinery could be seen to possess a number of advantages, including especially the ability to recover high purity lignin and other co-products, as well as disadvantages, including a higher number of prosessing steps, increased energy consumption and potentially lower yield compared to the more standard dilute acid pretreatment process. An economic analysis of the organosolv process was required to assess quantitatively whether the production of lignin and co-products would be enough to justify the abovementioned disadvantages, and the fifth research question was formulated to address these aspects. The economic analysis included the estimation of investment and operation costs and revenues from the sales of co-products. Economic feasibility was characterized by the minimum price of ethanol that is required to cover the costs of production and make a certain return on the invested capital (so called Minimum Ethanol Selling Price, MESP). The MESP of the organosolv process was furthermore compared to that of the reference dilute acid process to gain understanding of the relative competitiveness of the organosolv process.

## 1.4 Limitations of the scope of the study

Various limitations to the scope of the study were described in the previous three subchapters (1.1-1.3). These included: no other sugar-based bio-chemical than ethanol are considered, no company-specific information is taken into account in evaluating the two biorefinery concepts, and the hemicellulose-extracted kraft pulp is considered only from the perspective of paper-grade pulp. The effect of these limitations on the findings of the study are discussed in more detail in subchapter 6.5. The scope of the thesis has also other limitations.

Firstly, as a potential novel product, the potential applications of the lignin product produced in the organosolv process (organosolv lignin) are discussed briefly. However, no detailed attempt to evaluate the exact applications and price of the organosolv lignin are made. Rather, the economic feasibility of the organosolv biorefinery concept is examined by calculating a minimum ethanol selling price (MESP) for the produced ethanol on the basis of a hypothetical base case lignin price. By varying the lignin price in sensitivity analysis, the effect of the lignin price on the MESP is then evaluated quantitatively. This offers an insight concerning the price level of lignin required to make the organosolv process cost-competitive.

Secondly, regarding the hemicellulose extraction concept, the attractiveness of the process is assessed on the basis of qualitative, technical aspects related to the extraction process and its effects on pulp mill operation and pulp quality, as well as an analysis of existing literature. No quantitative economic analysis of the concept is carried out. Although the literature review of hemicellulose extraction (subchapter 3.1) covers different kinds of hemicellulose extraction methods, only the attractiveness of water prehydrolysis is evaluated in the thesis.

Thirdly, as the two studied biorefinery concepts are lignocellulosic biorefineries, no other feedstock types are considered in this work. The specific focus is on woody raw materials. Finally, the evaluation of the two concepts is purely technical (both concepts) and economic (the organosolv process). Other aspects, such as environmental or social, are not considered. The economic assessment of the organosolv process is furthermore comparative by nature: the cost competitiveness of the process is compared to the reference, dilute acid-based ethanol production process. In other words, markets and pricing of second generation ethanol and the profitability of an investment in the organosolv process are not analyzed in the thesis.

## 1.5 Outline of the thesis

The thesis consists of two parts, an overview and four research publications. The first part, the overview, presents the background of the thesis, the research objectives, a literature review on biomass fractionation and biorefinery concepts, the research design, a review of the research publications, as well as discussion and conclusions. The four research publications are then presented in the second part (note that Publication I is included only in the printed version of the thesis). Figure 3 presents the outline of the thesis, describing the main starting points (inputs) and outcomes (outputs) for each chapter.

Part I consists of seven chapters. The first chapter is an introduction, covering the background and positioning of the study, as well as the research objectives. The second chapter provides a literature review on biorefinery concepts. The concepts are classified into biochemical and thermochemical routes. A brief overview of pulp mill-based biorefinery concepts is also provided in the chapter. The third chapter offers a more detailed overview of the two biorefinery concepts studied in this thesis: hemicelluloses extraction prior to kraft pulping and organosolv pulping. The fourth chapter discusses the methodological approach adopted in the thesis. The fifth chapter contains a review and synthesis of the publications, followed by a more comprehensive discussion of the results in the sixth chapter. The seventh chapter summarizes the research and findings.

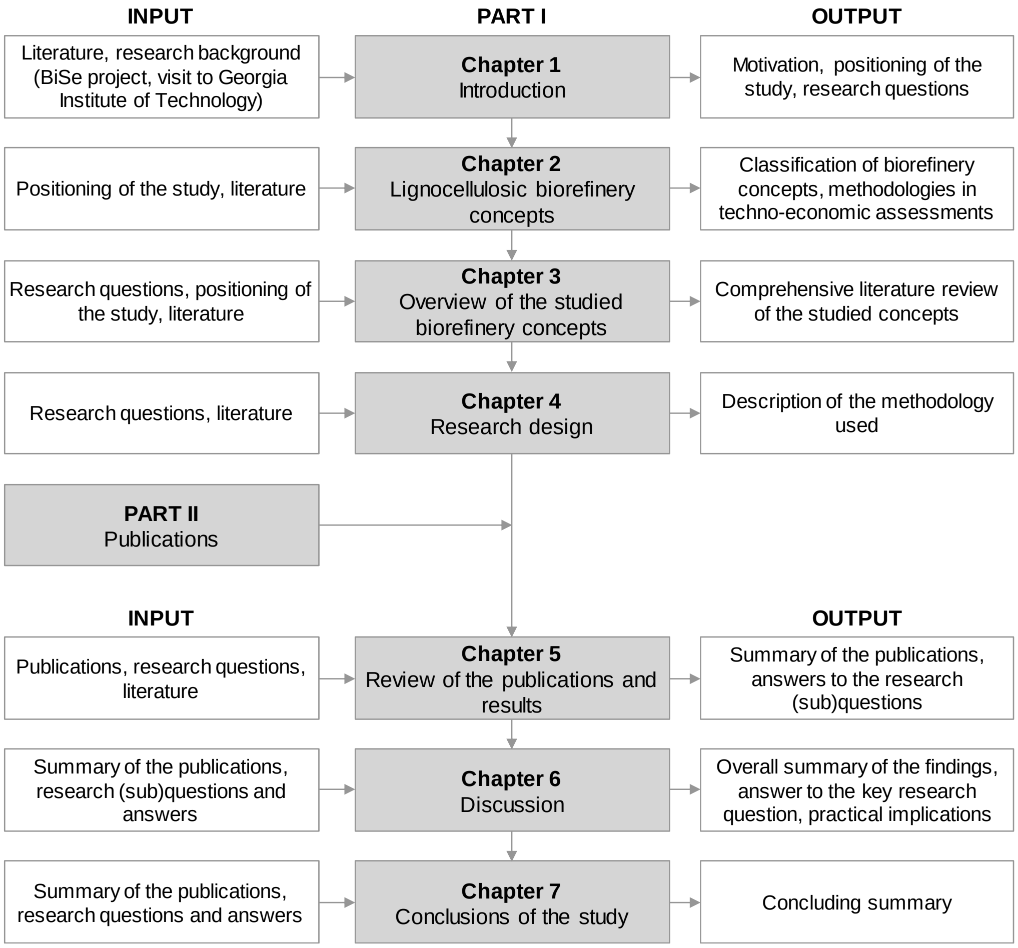


Figure 3: Outline of the thesis.

# 2 Lignocellulosic biorefinery concepts

As outlined in Chapter 1, the research carried out in this thesis focuses on the generation of bioethanol from woody (lignocellulosic) feedstock through the biochemical platform. This chapter provides an overview on various biochemical (subchapter 2.1) and thermochemical (subchapter 2.2) fractionation and biorefinery concepts. Since the focus in this thesis is on the production of lignocellulosic ethanol through a biochemical route (fermentation), the thermochemical processes are reviewed only very briefly. Although several of the reviewed biorefinery concepts can be used to produce also chemicals, the review has been carried out particularly from the perspective of the manufacture of liquid biofuels. In subchapter 2.1, the emphasis is primarily on pretreatment methods and secondarily on subsequent hydrolysis and ethanol manufacture. This is due to the nature of the two studied biorefinery concepts. Organosolv pulping is in this thesis evaluated as a pretreatment method prior to enzymatic hydrolysis. Although liquid hot water prehydrolysis is evaluated from the perspective of co-production of ethanol and paper-grade pulp, it could also be used as a pretreatment prior to hydrolysis. Furthermore, both process concepts aim at ethanol manufacture. As the organosolv concept is studied from the perspective of its techno-economic feasibility, subchapter 2.1.4 provides a brief and general overview of techno-economic assessments carried out on biochemical routes to lignocellulosic ethanol. Assessments specific to hemicellulose extraction prior to chemical pulping and organosolv pulping are in turn discussed in separate subchapters 3.1.4 and 3.2.4. Figure 4 below outlines the biochemical and thermochemical concepts reviewed in subchapters 2.1 and 2.2.

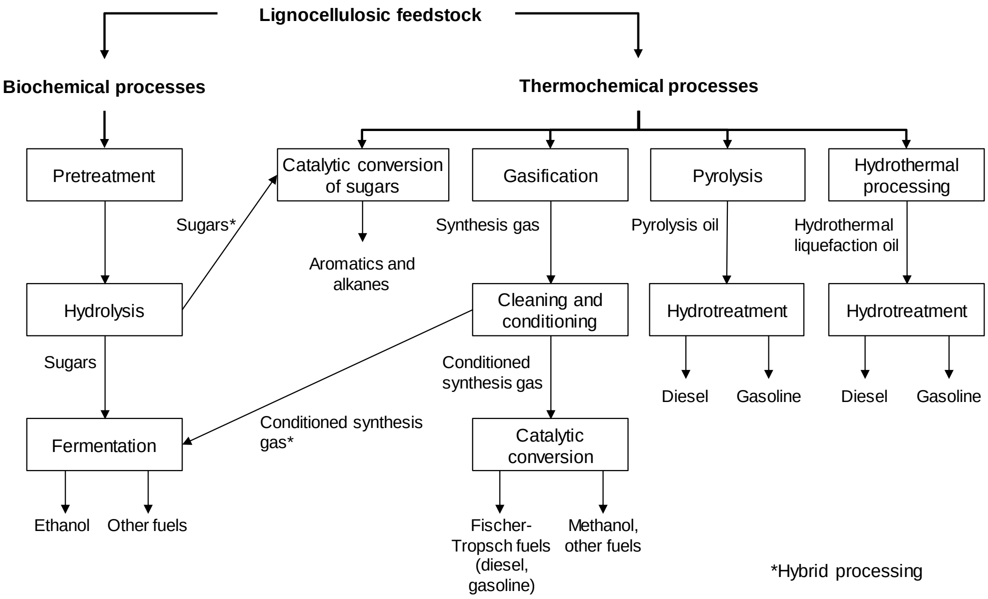


Figure 4: Overview of biochemical and thermochemical biorefinery concepts for liquid biofuel production.

In addition to an overview of biochemical and thermochemical biorefinery concepts provided in subchapters 2.1 and 2.2, biorefinery concepts integrated to pulp mills (subchapter 2.3) are also discussed briefly in this chapter.

## 2.1 Biochemical processes

In biochemical biorefinery processes, the carbohydrates present in the lignocellulosic feedstock are typically converted to sugars through pretreatment and hydrolysis, followed by fermentation of the sugars to fuels (such as ethanol) or chemicals.

### 2.1.1 Pretreatment

In their native state, plant cell walls are recalcitrant to microbial and enzymatic deconstruction (Himmel et al. 2007). The aim of pretreatment is to disrupt the cell wall structure to make it more accessible to enzymatic hydrolysis. While the exact effects of pretreatment on the lignocellulosic material differ between pretreatment methods (da Costa Sousa et al 2009; Chundawat et al. 2011), the key physicochemical effects of pretreatment from the perspective of enhanced enzymatic accessibility include cleavage of lignin carbohydrate complexes (LCC) and lignin modification and redistribution (Chundawat et al. 2011), as well as depolymerization and dissolution of hemicellulose and alteration of cellulose crystallinity (Mosier et al. 2005; Zheng et al. 2009; Chundawat et al. 2011).

Numerous pretreatment methods have been suggested in the literature. These methods can be classified into four general categories: physical, chemical, biological and solvent-fractionation methods (da Costa Sousa et al. 2009; Chundawat et al. 2011). In physical pretreatment methods, the particle size of plant material is decreased by mechanical stress. Specific physical methods include dry, wet and vibratory ball milling, as well as compression, hammer and disc milling. Physical size reduction increases the surface area to the volume ratio of plant material, thereby improving enzymatic hydrolysis. In principle, physical methods could therefore be used as a sole pretreatment method. Reducing the particle size beyond a certain particle size is, however, not economically feasible due to high energy consumption. Physical pretreatment is therefore used prior to other pretreatment methods particularly to improve mass and heat transport (da Costa Sousa et al. 2009; Ewanick and Bura 2010).

Chemical pretreatment methods include acidic, alkaline and oxidative pretreatment processes. In acidic methods, pretreatment is carried out in acidic conditions. These methods include dilute and concentrated acid, steam explosion and liquid hot water pretreatments. The acidic catalyst in pretreatment can be either an externally added acid (mineral acid such as sulphuric acid) or formed during the pretreatment by liberation of acetic acid through hydrolysis of hemicellulose acetyl linkages. Further, water itself acts as an acid at a high temperature. The acid catalyzes the hydrolytic cleavage of hemicellulose and lignin from the plant cell wall, resulting in partial solubilization of these two cell wall components, and consequently, improved enzyme accessibility (da Costa Sousa et al. 2009; Chundawat et al. 2010). The extent of hemicellulose and lignin solubilization depends considerably on the severity of the pretreatment, which in turn depends on the residence time, temperature and acidity (pH). Higher severity results in considerable hydrolysis of hemicellulose to monomeric sugars. Simultaneously, the generation of sugar and lignin degradation products, such as furfural, 5-hydroxymethylfurfural, levulinic acid, phenolic acids/aldehydes and other aliphatic acids, which can act as inhibitors in downstream biological processing, is also increased. Acidic pretreatment is therefore a trade-off between maximizing the enzymatic digestibility of cellulose and acid catalyzed hydrolysis of hemicelluloses to sugars, and minimizing the formation of inhibitory compounds (Chundawat et al. 2010). In dilute acid pretreatment, the acid (typically sulfuric acid) concentration is 0.5 – 5 % and the temperature 160 – 220 °C. Steam explosion is based on heating the biomass with high-pressure steam to a high temperature (160 – 290 °C) for a residence time ranging from a few seconds to several minutes, followed by a rapid release of pressure. Steam explosion can be run either with (most typically acid) or without an added catalyst. Liquid hot water pretreatment is in turn based on utilizing water at a temperature of 160 – 230 °C in liquid state (da Costa Sousa et al. 2009; Chundawat et al. 2010).

Alkaline catalysts are used in alkaline pretreatments. These chemicals typically reduce recalcitrance by catalyzing the cleavage of hemicellulose acetyl groups and lignin-carbohydrate complex linkages, thereby promoting the solubilization of lignin and hemicellulose from the biomass and reducing non-specific binding of enzymes (da Costa Sousa et al. 2009; Chundawat et al. 2010). One widely studied alkaline pretreatment method is ammonia fiber expansion (AFEX). In AFEX, liquid ammonia is added to pre-wetted biomass in the amount of 0.6 – 2 kg of ammonia per dry kg of biomass in a high-pressure reactor and cooked for 5 – 45 min at the relatively low temperature of 60 – 140 °C. After a set residence time, the pressure is released rapidly, enabling the recovery of volatile ammonia. The recovery of ammonia leaves the pretreated biomass as a dried, solid fraction with no separate liquid stream (da Costa Sousa et al. 2009; Chundawat et al. 2010). Other alkaline pretreatments include several other ammonia-based treatments (such as supercritical ammonia treatment, ammonia recycle percolation (ARP), soaking in aqueous ammonia and ammonia peroxide treatment), as well as lime and calcium hydroxide -based pretreatments (da Costa Sousa et al. 2009; Chundawat et al. 2010).

Oxidative pretreatments utilize oxidizing agents for the improval of enzymatic digestibility by reacting with lignin aromatics and alkyl/aryl ether linkages. Oxidative agents can, however, also react with hemicellulose and cellulose, decreasing the overall sugar yield. One type of oxidative pretreatment is alkaline wet oxidation, where the pretreatment is carried out in alkaline conditions at a high temperature of 170 – 220 °C, using pressurized air or hydrogen peroxide as the oxidizing agent. The alkali, sodium carbonate in this process concept, promotes the solubilization of hemicellulose and minimizes the formation of furan-based degradation products (da Costa Sousa et al. 2009). Biological pretreatments are normally carried out by utilizing fungi (such as white rot basidiomycetes) or certain actinomycetes, which secrete extracellular enzymes, such as lignin peroxidases and laccases, which help solubilize lignin. Biological pretreatments consume low amounts of energy but require long residence times, from several hours to days. Solvent fractionation pretreatment methods utilize solvents to solubilize various components of the plant cell wall. In addition to organosolv pretreatment, which will be discussed in detail in subchapter 3.2, solvent fractionation methods include phosphoric acid and ionic liquid fractionation (da Costa Sousa et al. 2009). Phosphoric acid fractionation utilizes a mixture of solvents (phosphoric acid, water, acetone and water), at a temperature of 50 °C to fractionate lignocellulosic biomass into amorphous cellulose, hemicellulose, lignin and acetic acid, based on the differences in solubility of these cell wall components in the different solvents. Some ionic liquids, containing usually anions of chloride, formate, acetate or alkyl phosphanate, are able to form hydrogen bonds with cellulose and solubilize cellulose, hemicelluloses and lignin at a temperature of 50 – 150 °C and biomass to ionic liquid ratio of 1:10 – 15. After dissolution, anti-solvents (such as water, methanol or ethanol) can be added to the mixture to recover cellulose (da Costa Sousa et al. 2009; Chundawat et al. 2010).

The different pretreatment methods have somewhat different effects on the pretreated substrate, from varying amounts of different biomass components solubilized during pretreatment to varying crystallinities and degrees of polymerization of cellulose. The different pretreatment methods have also a different response to enzymatic hydrolysis. Tables 1 and 2 below review the pretreatment conditions, their effects on the pretreated substrate and on the sugar yields from pretreatment and enzymatic hydrolysis. The feedstock in these experiments was poplar, obtained from a research project where the different pretreatment methods were evaluated on a systematic, comparable way (Wyman et al. 2009; Chundawat et al. 2010). In addition to data on the pretreatment studied in that project, the table includes data on the organosolv pretreatment of poplar. The organosolv pretreatment was based on using ethanol as a solvent and sulphuric acid as a catalyst (Pan et al. 2006). It should be noted that as the data on organosolv is derived from a different research setting (different batch of poplar used in the experiments, different type of enzyme and loading), the results are not fully comparable.

Table 1: Conditions applied in pretreatment and the effects of pretreatment on a poplar feedstock (dilute acid, $SO_2$ catalyzed steam explosion, controlled pH liquid hot water, AFEX, ARP and lime, based on Chundawat et al. (2010), organosolv based on Pan et al. (2006)).

|  | Pretreatment conditions |  |  |  | Biomass component removal in pretreatment (C:H:L:A)[1], wt % |  |  |  | Cellulose after pretreatment |  |
|---|---|---|---|---|---|---|---|---|---|---|
| Type of pretreatment | T (°C) | t (min) | Catalyst (g/g[2]) | Water (g/g[2]) | C[1] | H[1] | L[1] | A[1] | CI[3] | DOP[4] |
| Dilute acid | 190 | 1.1 | 0.02 $H_2SO_4$ | 3.3 | 10-15 | 90-95 | ND | 90 | 51 | 500 |
| $SO_2$ catalyzed steam explosion | 190 | 5 | 0.03 $SO_2$ | 4 | 1-5 | 90-95 | ND | 80-85 | 56 | 650 |
| Controlled pH liquid hot water | 200 | 10 |  | 5.67 | 1-5 | 55-60 | ND | 70-75 | 54 | 1800 |
| AFEX | 180 | 10 | 2 $NH_3$ | 2.3 | 0 | 0 | 0 | 70-80 | 48 | 2700 |
| ARP | 185 | 27.5 | 0.55 $NH_3$ | 3.2 | 5-10 | 30-35 | 40 | 85 | 50 | 3200 |
| Lime[5] | 160 | 120 | 0.2 $Ca(OH)_2$ | 1.6 | 1-3 | 3-5 | 50 | 95 | 55 | 1600 |
| Organosolv | 180 | 60 | 0.0125 $H_2SO_4$ | 6.5[6] | 12[7] | 81[8] | 73 |  |  |  |

[1] C:H:L:A = Cellulose:Hemicelluloses:Lignin:Acetyl groups
[2] g/g dry biomass
[3] The cellulose crystallinity index (CI). The index of untreated poplar is 50
[4] The degree of polymerization (DOP). DOP of untreated poplar cellulose is 3500
[5] In the presence of pressurized $O_2$
[6] 3.6 g/g water, 2.9 g/g ethanol
[7] Glucose removal
[8] Xylose removal

Table 2: Xylose and glucose yields in pretreatment (denoted as Stage 1) and enzymatic hydrolysis (Stage 2). Dilute acid, $SO_2$ catalyzed steam explosion, controlled-pH liquid hot water, AFEX, ARP and lime, based on Wyman et al. (2009), with enzymatic hydrolysis carried out at cellulase loading of 15 filter paper units (FPU)/g glucan in the original feedstock; and organosolv based on Pan et al. (2006), with 20 FPU cellulase/g cellulose. The single values in the table stand for monomer sugar yield, whereas in the case of two values the first stands for total (monomeric and oligomeric) and the second for monomeric sugar yield.

| | Xylose yield, wt-% | | | Glucose yield,wt- % | | | Total sugars, wt-% | | |
|---|---|---|---|---|---|---|---|---|---|
| Type of pretreatment | Stage 1 | Stage 2 | Total | Stage 1 | Stage 2 | Total | Stage 1 | Stage 2 | Total |
| Dilute acid | 62 | 9 | 72 | 24 | 63 | 87 | 34 | 49 | 83 |
| $SO_2$ catalyzed steam explosion | 74/54 | 9 | 84/64 | 3 | 97 | 100 | 22/16 | 74 | 96/91 |
| Controlled pH liquid hot water | 58/4 | 38 | 96/41 | 0/2 | 54 | 56/54 | 17/1 | 50 | 66/51 |
| AFEX | 0 | 52 | 52 | 0 | 53 | 53 | 0 | 53 | 53 |
| ARP | 37/0 | 32/31 | 69/31 | 1/0 | 49/49 | 49/49 | 10/0 | 45/44 | 54/44 |
| Lime[4] | 5/0 | 73/65 | 78/65 | 0 | 96/91 | 96/91 | 1/0 | 90/84 | 91/84 |
| Organosolv | 35/15 | ND | 35/15 | 1[1] | 86 | 87 | 10/5 | 63 | 73/67 |

[1] Oligomeric/monomeric composition of the dissolved glucose was not presented in the study of Pan et al. (2006)

As can be seen in Tables 1 and 2, there are differences in the effects of different pretreatment technologies both on the feedstock and on the subsequent enzymatic hydrolysis. The chemical pretreatments carried out in an acidic environment (in these tables dilute acid, $SO_2$ catalyzed steam explosion and liquid hot water) and organosolv pretreatment (where the environment is acidic) generally result in considerable dissolution of hemicelluloses. Correspondingly, the monomeric and oligomeric xylose (major type of hemicellulose sugar) yields are high in the pretreatment step. In alkaline pretreatments (AFEX, ARP and lime) the dissolution of hemicelluloses is generally lower, with AFEX notably resulting in practically no dissolution of hemicelluloses.

Alkaline (apart from AFEX) and organosolv pretreatments dissolve lignin in considerable amounts.

In the enzymatic hydrolysis step, the glucose yields varied from lower, approximately 50 %, in liquid hot water, AFEX and ARP to higher, in the range of 60 to above 90 %, in the other pretreatments. Comparing the sugar yields of different pretreatment methods, it should be noted that the yield depends on the type and amount of the enzyme applied, and the optimal enzyme cocktails may vary between the pretreatment methods (Wyman et al. 2009). For example, as reported by Kumar and Wyman (2009), the addition of xylanases to enzymatic hydrolysis increased sugar yields of poplar treated by all types of pretreatments, with a particularly considerable improvement seen with AFEX pretreatment. Further, feedstock has a considerable effect on overall sugar yields. In the research project in which the data presented in Tables 1 and 2 was obtained, the sugar yields were generally considerably higher with corn stover than with poplar (Chundawat et al. 2010). The fermentation of sugars produced by enzymatic hydrolysis of washed poplar solids after pretreatment by glucose/xylose co-fermenting yeast strain resulted in ethanol yields (on enzyme hydrolyzed sugars) that were generally somewhat higher for higher pH pretreatments (Wyman et al. 2009). The total ethanol yield would, however, depend on both the sugar yield and inhibitor generation in pretreatment (if the liquid stream from pretreatment is fermented), the sugar yield in enzymatic pretreatment, and the overall fermentation yield. Different pretreatment processes are furthermore associated with different operating and capital expense levels (see subchapter 2.1.4), having an impact on the competitiveness of different pretreatment technologies.

### 2.1.2 Hydrolysis

After the pretreatment step, the polysaccharides present in the pretreated biomass are hydrolyzed to fermentable sugars. In enzymatic hydrolysis, cellulose is broken down to sugars by a combined activity of different cellulase enzymes. The key cellulases active in this bioconversion are cellobiohydrolases, endoglucanases and ß-glucosidase. Cellobiohydrolases hydrolyze the ends of cellulose chains, generating cellobiose as their main product. Endoglucanases, in turn, cleave the cellulose chain from a random, typically amorphous, location along the length of the chain, and ß-glucosidase hydrolyzes cellobiose to D-glucose. As the pretreated biomass generally contains also residual hemicelluloses, the addition of hemicellulases and ß-xylosidase (hydrolyzing short xylooligosaccharides to xylose) to the cellulase mixture typically improves the enzymatic hydrolysis (Quinlan et al. 2010; Van Dyk and Pletschke 2012). Cellulase enzymes can be produced by fungi (including particularly the widely utilized *Trichoderma Reesei*) and bacteria. In addition, cellulose-producing species can also be found among archea, plants and insects. Fungus-based cellulase production processes are generally considered as the most economically promising ones (Quinlan et al. 2010).

In addition to enzymatic hydrolysis, hydrolysis can also be carried out chemically by using dilute or concentrated acids. Dilute acid hydrolysis is typically carried out by using sulfuric acid at a concentration of 0.5 – 1 % at a temperature of 140 – 190 °C, while concentrated acid hydrolysis uses a higher acid concentration of approximately 70 %, and a considerably lower temperature. Major drawbacks in dilute acid hydrolysis are the degradation of generated sugars and the generation of inhibitory compounds. A key challenge in the concentrated acid process is in recycling the acid economically (Shahbazi et al. 2010).

### 2.1.3 Fermentation and product recovery

The hydrolysate from the hydrolysis stage contains both six-carbon (C6, hexoses, particularly glucose) and five-carbon (C5, pentoses, particularly xylose) sugars. These sugars can be fermented to ethanol by various yeast and bacteria strains (Balat 2011; Demeke et al. 2013). The most widely used microorganism for first generation ethanol production is the yeast *Saccharomyces cerevisiae* (baker’s yeast), due to its efficiency and high tolerance to ethanol and inhibitors (Runquist et al. 2010; Demeke et al. 2013). The yeast does, however, lack the natural ability to utilize pentose sugars, and metabolic engineering has been applied to provide baker’s yeast with this ability (Balat 2011; Demeke et al. 2013). In addition to baker’s yeast, strain development for the fermentation of lignocellulosic sugars has been carried out also for other microorganisms, including bacteria (such as *Escherichia coli, Zymomonas mobilis* and *Klebsiella oxytoca*) and other yeasts (including naturally xylose fermenting yeasts such as *Pichia Stipitis*) (Balat 2011; Demeke et al. 2013).

In addition to a separate fermentation stage following enzymatic hydrolysis, both simultaneous saccharification and fermentation (SSF, where enzymatic hydrolysis is carried out in the same stage as fermentation) and consolidated bioprocessing (CBP, where cellulase production, enzymatic hydrolysis and fermentation are carried out in one stage by one microbial community) are being developed (Manzanares 2010). The produced ethanol after fermentation can be recovered and dewatered by distillation and molecular sieves (Humbird et al. 2011).

In addition to ethanol, also numerous other fuels and chemicals can be produced by fermentation, including n-butanol and iso-butanol, as well as lactic acid, succinic acid and adipic acids (de Jong et al. 2012). Furthermore, the produced sugars can be converted catalytically to fuels or chemicals (see subchapter 2.2.4).

### 2.1.4 Techno-economic assessments of lignocellulosic ethanol

Numerous techno-economic assessments for the evaluation of different biofuel-producing biorefinery concepts have been presented in the literature. The studies consist generally of a conceptual level process design, followed by material and energy balance calculations, investment and operating cost estimations and discounted cash flow projections. Economic feasibility is often characterized by the minimum ethanol selling price (MESP) (Humbird et al. 2011) or a similar minimum fuel selling price. The minimum fuel price is defined as the plant-gate price of the fuel, resulting in a net present value (NPV) of zero with a given discount rate after taxes. In other words, all cash flows, including revenues, capital investment, variable and fixed costs and taxes, are discounted to the present day with a certain discount rate. The selling price of the ethanol is then iterated until the sum of all discounted cash flows (net present value) is zero. This resulting price is the MESP. The minimum selling price can be used specifically to compare different process alternatives against each other, but it can also be used to evaluate the economic attractiveness of a process on the market (by comparing the minimum selling price to the actual market price) (Humbird et al. 2011). In addition to such cost-based minimum selling price calculations, also various other metrics, such as internal rate of return (IRR) can be used in evaluating biorefinery concepts. This subchapter provides a brief overview of techno-economic assessments of biochemical routes to lignocellulosic ethanol.

In the manufacture of lignocellulosic bioethanol through the biochemical route, the key cost contributors are generally the capital, feedstock and enzyme costs (see e.g. Humbird et al. 2011). Numerous techno-economic assessments on lignocellulosic ethanol have been published, with a relatively large variety in the resulting MESPs. The review of techno-economic studies published between 2008 and 2011 presented in the study of Humbird et al. (2011) found MESPs to vary in the range of 0.6 and 4.6 USD/gallon (0.2 to 1.2 USD/L), with assumptions related to feedstock prices, process yields, enzyme costs, factors related to capital costs and co-product sales explaining most of the variation (Humbird et al. 2011). Table 3 below reviews a short list of techno-economic studies on lignocellulosic bioethanol.

Table 3: Techno-economic assessments of lignocellulosic ethanol.

| Reference | Pre-treatment[1] | Feedstock type[2], price (USD/dry t) and ethanol yield (L/dry t) | Capacity (million L/a) | Inv. cost (MUSD), cost year | Enzyme cost (USD/L) | MESP (USD/L) |
|---|---|---|---|---|---|---|
| Humbird et al. 2011 | Dilute acid | Corn stover, 64.5, 330 | 230 | 420 (2007) | 0.09 | 0.57 |
| Tao et al. 2011 | AFEX | Switchgrass, 76.6, 275 | 192 | 348 (2007) | 0.07 | 0.72 |
| Tao et al. 2011 | Dilute acid | Switchgrass, 76.6, 270 | 189 | 349 (2007) | 0.07 | ~0.74 |
| Tao et al. 2011 | Lime | Switchgrass, 76.6, 252 | 177 | 385 (2007) | 0.07 | ~0.83 |
| Tao et al. 2011 | Liquid hot water | Switchgrass, 76.6, 217 | 152 | 325 (2007) | 0.07 | ~0.87 |
| Tao et al. 2011 | Soaking in aqueous ammonia | Switchgrass, 76.6, 185 | 130 | 364 (2007) | 0.07 | 1.08 |
| Tao et al. 2011 | $SO_2$ catalyzed steam explosion | Switchgrass, 76.6, 282 | 198 | 340 (2007) | 0.07 | ~0.78 |
| Kazi et al. 2010 | Dilute acid | Corn stover, 83, 289 | 202 | 376 (2007) | 0.19 | 0.91 |
| Kazi et al. 2010 | 2-stage dilute acid | Corn stover, 83, 177 | 124 | 391 (2007) | | 1.17 |
| Kazi et al. 2010 | Liquid hot water | Corn stover, 83, 211 | 148 | 327 (2007) | | 1.18 |
| Kazi et al. 2010 | AFEX | Corn stover, 83, 250 | 175 | 386 (2007) | | 0.98 |

[1] Apart from the 2-stage dilute acid pretreatment studied in Kazi et al. (2010), all the ethanol production processes studied in the reviewed articles assumed enzymatic hydrolysis

[2] The amount of feedstock was 2000 dry t/d in all of the studied processes

The technoeconomic studies reviewed above all assumed a feedstock rate of 2000 dry t/d, with Humbird et al. (2011) and Kazi et al. (2010) assuming corn stover and Tao et al. (2011) assuming switchgrass as the feedstock. The yields, and consequently the ethanol production outputs as well as investment costs, varied somewhat between the reviewed studies and different pretreatment steps assumed within the two studies that evaluated different pretreatment processes (Tao et al. 2011 and Kazi et al. 2010). Humbird et al. (2011) assumed an ethanol yield of 330 L/t of corn stover, based on dilute acid pretreatment, while Tao et al. (2011) and Kazi et al. (2010) assumed generally lower yields in the approximate range of 180 to 290 L/t. Investment costs were found to be in the approximate range from 330 MUSD to 420 MUSD, with the boiler and turbogenerator generally found to be the single most expensive process section (Kazi et al. 2010; Humbird et al. 2011). Other major capital cost items included pretreatment, saccharification and fermentation (Kazi et al. 2010; Humbird et al. 2011), as well as wastewater treatment (Humbird et al. 2011). Investment costs differed somewhat between pretreatment methods. Variations between the MESPs of different pretreatments were, however, mainly a result of differences in yields: higher yields of dilute acid and AFEX (Kazi et al. 2010; Tao et al. 2011), as well as $SO_2$ catalyzed steam explosion (Tao et al. 2011) resulted in lower MESPs. As discussed in subchapter 2.1.1, it should be noted that the type of enzyme cocktail and feedstock have an effect on the sugar (and consequently ethanol) yield differences between pretreatment technologies. Assumptions concerning the feedstock and enzyme cocktail can therefore have an effect when pretreatment methods are evaluated against each other. Overall, the MESPs ranged from a low 0.57 USD/L (2.15 USD/gal) (dilute acid, Humbird et al. 2011) to a high 1.18 USD/L (4.5 USD/gal) (liquid hot water, Kazi et al. 2010). The enzyme costs in these studies ranged between 0.07 USD/L (0.25 USD/gal) (Tao et al. 2011) and 0.19 USD/L (0.71 USD/L) (Kazi et al. 2010).

## 2.2 Thermochemical processes

While biochemical processes utilize enzymes and microorganisms for the conversion of biomass into fuels or chemicals, thermochemical conversion uses heat and typically also catalysts for the conversion. Thermochemical processing routes include gasification, pyrolysis, hydrothermal processing and catalytic conversion of sugars (Brown 2011). Since the focus in this thesis is on the production of lignocellulosic ethanol through fermentation (a biochemical route), the thermochemical processes are discussed only very briefly.

In gasification, carbon-containing feedstocks are converted under an elevated temperature and low oxygen content to synthesis gas (also called producer gas) in a gasifier. The gas is cleaned and conditioned prior to use, with the degree of cleaning and conditioning depending on the application. The potential applications include combined heat and power, as well as synthetic liquid fuels, such as Fischer-Tropsch fuels (diesel, gasoline) and methanol (Bain and Broer 2011). Pyrolysis of biomass is carried out in oxygen-free conditions at atmospheric pressure (Venderbosch and Prins 2011). Through thermal decomposition, the process generates three fractions, liquid, gas and char. The yields of each fraction depend considerably on the process conditions (Bridgwater 2012). The conditions in a so-called fast pyrolysis process, moderate temperature and short vapor residence time, promote the generation of a liquid product (called bio-oil or pyrolysis oil) (Venderbosch and Prins 2011; Bridgwater 2012). The pyrolysis oil can be used as a fuel e.g. in boilers or furnaces. Alternatively, the pyrolysis oil could potentially also be upgraded to liquid transportation fuels, such as diesel and gasoline (Bridgwater 2012).

In hydrothermal processing, biomass in a water slurry is treated under elevated temperature and pressure. The process is typically carried out at subcritical conditions, with temperature and pressure in the range of 250 – 374 °C and 4 – 22 MPa (Elliot 2011). Hydrothermal liquefaction, a subcategory of hydrothermal processing, is carried out at a lower end of the abovementioned temperature range, and results in the formation of an oil stream. An alkali catalyst, promoting base-catalyzed condensation reactions which can result in the formation of aromatic oils, is typically used in the process. In addition to oil, hydrothermal processing results in the formation of gas and aqueous residue streams. The oil can be used as a heavy fuel oil (Elliot 2011) or converted to liquid fuels such as diesel or gasoline (Elliot 2007; Elliot 2011). While the hydrothermal processing of biomass relies on high temperature for the conversion of biomass to liquid or gaseous products, the sugars present in the biomass can be catalytically converted to fuels or chemicals by using milder reaction conditions (Tompsett et al. 2011). One type of catalytic conversion is aqueous phase reforming. In this process, the sugars or other oxygenated molecules in the aqueous solution are converted catalytically to $H_2$, shorter or longer chain alkanes and aromatics under a temperature and pressure of 177 – 302 °C and 1 – 10 MPa. As sugars have low thermal stability, they need to be converted to polyols (e.g. glucose to sorbitol) before reforming reactions to reduce coke formation (Tompsett et al. 2011; Blommel and Cortright 2008).

In addition to the main thermochemical routes to fuels and chemicals described above, there are also hybrid routes that combine biochemical and thermochemical processing. One such hybrid route is the gasification of biomass (thermochemical step) followed by fermentation of the produced synthesis gas (biochemical step) (Choi 2011). Also other routes could in principle be called hybrid routes, such as the conversion of sugars liberated from biomass by enzymatic hydrolysis (biochemical step), followed by the abovementioned catalytic conversion of the sugars (thermochemical step) to chemicals or fuels (Brown 2011).

## 2.3 Pulp mill biorefinery concepts

### 2.3.1 Brief description of kraft pulping

As mentioned in subchapter 1.2, a chemical pulp mill, converting wood to pulp, electricity and by-products, can in principle be considered as a lignocellulosic biorefinery. The dominating chemical pulping process is the so-called kraft process (also called the sulfate process) where wood chips are cooked with an aqueous mixture, called white liquor, of sodium sulfide and sodium hydroxide at an elevated temperature in the range of 140 – 175 °C. The cooking dissolves approximately 90 % of the lignin present in the wood chips, while also degrading a considerable amount of hemicelluloses and some cellulose. The pulp from the digester is washed and bleached (Sixta et al. 2006).

The black liquor, consisting of the dissolved organics and spent cooking chemicals, is in turn evaporated and combusted in a recovery boiler for the generation of steam and electric power as well as recovery of cooking chemicals. The smelt from the recovery boiler, containing mainly sodium carbonate and sodium sulfate, is dissolved in water to produce a so-called green liquor. After clarification or filtration, the green liquor is fed to slaking (conversion of burned lime (CaO) to calcium hydroxide (slaked lime)) and causticizing (conversion of sodium carbonate from the smelt with slaked lime to produce sodium hydroxide and calcium carbonate). After the generated calcium carbonate is separated from the liquor, the resulting white liquor is fed back to cooking. The lime (calcium carbonate) is reburned in a lime kiln to produce burned lime that can be fed back to slaking (Krotscheck and Sixta 2006; Sixta et al. 2006). Figure 5 in subchapter 2.3.2 below presents a simplified block diagram of a conventional kraft pulp mill, along with more novel biorefinery processes.

### 2.3.2 Biorefinery processes integrated to a pulp mill

In addition to the conventional chemical pulp mill, various variations have been studied that would integrate novel biorefinery processes to the mill and expand its product portfolio to novel bio-based fuels, chemicals or materials. Some of the widely studied biorefinery concepts include the separation of hemicelluloses prior to cooking, separation of lignin from black liquor, gasification of black liquor, and conversion of tall oil to biodiesel, as well as various ways to process bark or other biomass (such as gasification to replace lime kiln fuel) (see e.g. Wising and Stuart 2006; Hamaguchi et al. 2012). Figure 5 presents a block diagram of a conventional kraft pulp mill, with the abovementioned technologies presented as possible additional process steps.

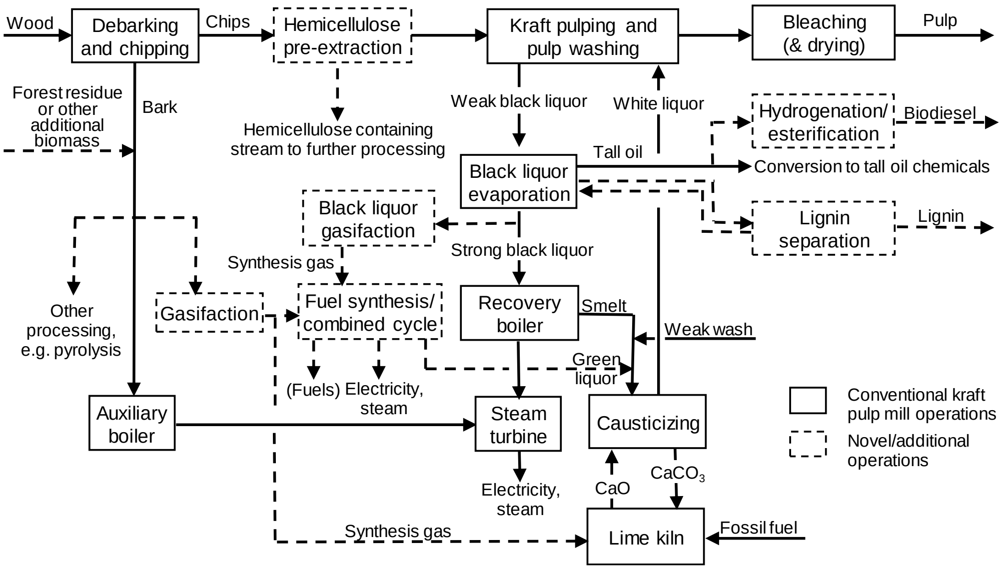


Figure 5: Block diagram of a conventional pulp mill and additional process steps (partially based on Hamaguchi et al. 2012).

Of the biorefinery process steps presented in the figure above, separation of lignin from black liquor can be carried out by precipitation by using carbon dioxide (Axegård 2007). The separated lignin can be used as a fuel (e.g. in a pulp mill lime kiln) or as a feedstock to chemicals and materials (Axegård 2007; Tomani 2010). One application area for kraft lignin that is currently in active development is its use in phenolic resins (see. e.g. Stora Enso 2016; UPM-Kymmene 2016). The separation of lignin has been implemented in the industrial scale (see e.g. Metso 2013). Gasification of black liquor has been piloted in various mills. The gasification can be carried out either as a so-called low temperature (inorganics as a solid) or high temperature (inorganics as a molten smelt) gasification. Piloted gasifier systems have included both entrained flow and fluidized bed designs. The produced synthesis gas could be used for electricity and heat generation through a combined cycle or converted catalytically to e.g. Fischer-Tropsch fuels or methanol (see subchapter 2.2) (Naqvi et al. 2010). Cooking chemicals are recovered by separating inorganic material from the synthesis gas and dissolving them to produce green liquor. The key issues with black liquor gasification include material corrosion in a very aggressive atmosphere of high temperatures and alkalinity, as well as increased load in the recausticizing and the lime kiln (Hamaguchi et al. 2012). In addition to the two ways to process black liquor presented above, lignin separation and gasification, also other ways have been suggested, including hydrogenation of black liquor (McKeough and Johansson 1987; Elliot and Oasmaa 1991; Oasmaa 1991) and separation of hydroxy acids (see e.g. Hellstén 2013).

Crude tall oil, a by-product of kraft pulping of mainly coniferous trees, is separated from black liquor as a soap by skimming, followed by acidification. The crude tall oil can be fractionated by distillation and utilized for various chemical and material end-uses (Gullichsen and Lindeberg 1999). An alternative route would be to produce renewable diesel from tall oil, either by esterification or hydrogenation (Wising and Stuart 2006). A particular focus has been on the hydrogenation route that was commercialized recently (UPM-Kymmene 2015). In addition to gasification, bark and other biomass (such as forest residues) can in principle be converted at a pulp mill site by various biorefinery processes to various solid and liquid fuels (see also Hamaguchi et al. (2012) for a review of options to process woody feedstocks at pulp mills).

Hemicellulose pre-extraction (in the form of prehydrolysis) is widely used in the manufacture of dissolving pulp. It has also been studied as a process step in the manufacture of paper-grade pulp. Hemicellulose pre-extraction, coupled with paper-grade pulp production is the process evaluated in this thesis, and it is discussed closer in subchapter 3.1. The other evaluated process is organosolv cooking, discussed in subchapter 3.2. Instead of pulp production, it is evaluated as a pretreatment step for bioethanol manufacture. Also kraft cooking could in principle be used as a pretreatment step, and repurposing an existing kraft pulp as a bioethanol plant has been suggested (see e.g. Phillips et al. 2008). Concerning the generation of fuels and chemicals, it should finally be pointed out that sulphite pulping, the second major chemical wood pulping method after kraft pulping, generates sugars as a pulping by-product (Sixta et al. 2006), providing a platform for biorefinery operations. Both the recovery of xylose and the fermentation of the spent pulping liquor to ethanol are being carried out in industrial scale (IEA 2009).

# 3 Overview of the studied biorefinery concepts

Chapter 3 provides a literature review of the two biorefinery processes studied in this thesis, hemicellulose extraction prior to kraft pulping and organosolv pulping. Both of the studied concepts are pulping-based multi-product biorefinery concepts.

## 3.1 Hemicellulose extraction prior to kraft pulping

### 3.1.1 Background and introduction

In hemicellulose extraction, a fraction of the wood material is extracted from wood chips prior to pulping. As a prehydrolysis step, hemicellulose extraction is conventionally practiced in the production of dissolving pulp. Dissolving pulp is a high-purity (low hemicellulose content) cellulose product that is used in the production of viscose or specialty-grade cellulose products (Sixta 2006). In dissolving pulp production, the prehydrolysis step is typically carried out in the steam phase based on batch cooking technology (Leavitt et al. 2012; Sixta et al. 2013). Recently, a continuous system based on (liquid) water (in this thesis the term water prehydrolysis refers to water prehydrolysis carried out with liquid water) was also commercialized (Leavitt et al. 2012).

Carried out partially, and either in the liquid water phase or by carrying out specific prehydrolyzate recovery in steam prehydrolysis, hemicellulose extraction could enable the recovery of the hemicellulose-containing stream (called prehydrolyzate in the prehydrolysis step) and the production of paper-grade pulp. In kraft pulping, a majority of hemicelluloses are dissolved and combusted in a kraft recovery boiler. As hemicelluloses have relatively low heating value, recovering them partially prior to pulping and converting them to fuels, chemicals or materials could offer an opportunity to increase the value of the hemicelluloses. The recovered hemicelluloses could be converted to monomeric sugars and fermented to ethanol or other chemicals. Various materials, such as films and coatings (Hansen and Plackett 2008) could also be produced from the extracted hemicelluloses.

Several methods have been suggested for the partial extraction of hemicelluloses in combination with paper-grade pulp production. In the prehydrolysis processes, hemicelluloses are hydrolyzed in acidic conditions at a high temperature to oligomeric and monomeric sugars and dissolved in the prehydrolyzate. Prehydrolysis can be carried out either by using pressurized hot water (called e.g. water prehydrolysis or auto-hydrolysis) (Wafa Al-Dajani et al. 2009; Mendes et al. 2009; Casebier and Hamilton 1969; Colodette et al. 2011; Garrote and Parajó 2002; Yoon et al. 2008; Leschinsky et al. 2009; Richter 1956),with the hydrolysis reaction catalyzed by acetic acid originating from the cleavage of acetyl groups from the xylan backbone, or by using a dilute solution of a mineral acid (e.g. $H_2SO_4$) as an additional catalyst of hydrolysis (Frederick et al. 2008; Parajó et al. 1994; Wafa Al-Dajani et al. 2009; Mendes et al. 2009; Richter 1956). Also extraction with steam has been studied, with or without an added acid catalyst (San Martín et al. 1995). In higher pH conditions, the extraction of hemicelluloses has been studied by using green liquor in a so-called near-neutral process (Mao et al. 2010), with strong alkali solutions at low temperatures (Wafa Al-Dajani and Tschirner 2008) or with white liquor (Helmerius et al. 2010). In addition to extracting hemicelluloses from wood chips prior to kraft pulping, also other possibilities for the recovery of hemicelluloses in combination with pulp production exist, including the extraction of hemicelluloses after pulping, from bleached pulp by using an alkaline solution (Saukkonen et al. 2012a), or separation from the cooking liquor (Axelsson et al. 1962). In this thesis, only the extraction of hemicelluloses from wood chips prior to pulping is covered. Specific focus is on the separation of hemicelluloses through water prehydrolysis and on the production of ethanol from the extracted hemicelluloses. While two of the articles included in this thesis (Publications I and II) focus on using softwood as raw material for hemicellulose extraction and pulping, the review will cover the use of both hardwoods and softwoods.

The viability of hemicellulose extraction -based co-production of paper-grade pulp and ethanol or other fuels and chemicals depends considerably on the effect of hemicellulose extraction on the yield and quality of the pulp and pulp mill operation, as well as the amount and quality of the hemicellulose-containing prehydrolyzate. The following subchapters present a literature review on these aspects of hemicellulose extraction.

### 3.1.2 Effects of hemicellulose extraction on pulp mill operation and pulp quality

One of the key aspects in evaluating the hemicellulose extraction concept is its effect on the yield in pulping. Changes in the yield on wood after pulping would affect either the production output (assuming that wood consumption is kept fixed) or wood consumption (assuming that pulp production is kept fixed). Such changes would affect the economic feasibility of the overall concept considerably, and also have an effect on the operation of various pulp mill subprocesses. For this reason, the effect of hemicellulose extraction on the yield in pulping is reviewed first, followed by discussion on the effects on the fiberline, chemical recovery and the quality of pulp.

#### Effects on yield and cooking

Water and dilute acid prehydrolysis processes, carried out in acidic conditions, have been found to decrease yield on wood after pulping (mass of brown stock pulp/mass of wood chips prior to extraction) considerably, while alkaline conditions result in similar yields on wood. Table 4 below provides a review of recent studies on acidic and alkaline hemicellulose extraction combined with kraft pulping.

Table 4: Review of a selected list of recent hemicellulose extraction studies.

| Extraction method and reference | Wood type | Extraction conditions (Extracting liquor[1], T, t, LTW[2], washing) | Extraction yield (on dry wood), composition of the extract | Pulping conditions (H-factor, Max T, sulfidity, EA[3]) | Yield on wood after cooking (kappa) |
|---|---|---|---|---|---|
| **Water prehydrolysis** | | | | | |
| Wafa Al-Dajani et al. 2009 | Aspen | 150 °C, 4.5 h, 4:1, washing | 19.0 %, of which 61 % carbohydrates (47 % xylan) | Ref: 768, 170 °C, 25 %, 21 %<br>Extracted: 308, 170 °C, 25 %, 21 % | Ref: 53.3 % (17.2)<br>Extracted: 40.9 % (12.5) |
| Colodette et al. 2011 | Eucalyptus | 150 °C, max. 60 min, 3.5:1, no washing | 16.2 % (at 60 min), of which 46 % xylan | Ref: 680, 155 °C, 37 %, 15.9 %<br>Extracted: 680, 155 °C, 37 %, 15.4 % | Ref: 53.9 % (16.9)<br>Extracted: 37.3 % (16.8) |
| Helmerius et al. 2010 | Birch | 150 °C, 90 min, 3:1, no washing | 8 %, with 11.75 g/L xylan in the prehydrolyzate | Ref: 500, 160 °C, 37 %, 21 %<br>Extracted: 365, 160 °C, 37 %, 21 % | Ref: 51.7 % (17.9)<br>Extracted: 46.9 % (16.7) |
| Mendes et al. 2009 | Eucalyptus globulus | 150 °C, 180 min, 4:1, washing | 12.5 %, with 16 g/L sugars in the prehydrolyzate after a post-hydrolysis step | Ref: 740, 160 °C, 28 %, 17.8 %<br>Extracted: 240, 28 %, 17.8 % | Ref: 54.7 % (13.1)<br>Extracted: 45.0 % (13.1) |

| Extraction method and reference | Wood type | Extraction conditions (Extracting liquor[1], T, t, LTW[2], washing) | Extraction yield (on dry wood), composition of the extract | Pulping conditions (H-factor, Max T, sulfidity, EA[3]) | Yield on wood after cooking (kappa) |
|---|---|---|---|---|---|
| Yoon and van Heiningen 2008 | Loblolly pine | 170 °C, 25 min, 4.5:1, no washing | 7.9 % | Ref: 170 °C, 30 %, 21.9 %<br>Extracted: 170 °C, 30 %, 19.4 % | Ref: ~45.5 % (30)<br>Extracted: ~39.5 % (30) |
| Duarte et al. 2011 | Sugar maple | 160 °C, 60 min, 4:1, washing | 14.4 % | Ref: ~820, 25 %, 18.1 %<br>Extracted: ~430, 25 %, 18.1 % | Ref: 54.5 % (24.8)<br>Extracted: ~45.2 % (25.8) |
| Kautto et al. 2010a | Scots pine | 150 °C, 101 min, 5:1, no washing[4] | 14.1 %, of which 48 % carbohydrates | Ref: 1450, 160 °C, 40 %, 18.8 %<br>Extracted: 1000, 160 °C, 40 %, 18.8 % | Ref: 46.2 % (33)<br>Extracted: 40 % (36) |
| Saukkonen et al. 2012b | Scots pine | 150 °C, 93 min[5], 4.6:1, no washing[5] | 11.5 % | Ref: 1600, 160 °C, 35 %, 20 %<br>Extracted: 1250, 160 °C, 35 %, 20.8 % | Ref: 46.9 % (25.4)<br>Extracted: 42.1 % (27.7) |

| Extraction method and reference | Wood type | Extraction conditions (Extracting liquor[1], T, t, LTW[2], washing) | Extraction yield (on dry wood), composition of the extract | Pulping conditions (H-factor, Max T, sulfidity, EA[3]) | Yield on wood after cooking (kappa) |
|---|---|---|---|---|---|
| **Acid prehydrolysis** | | | | | |
| Mendes et al. 2009 | E. globulus | $H_2SO_4$ at 0.4 wt-% on wood, 140 °C, 120 min, 4:1, washing | 13.1 % with 36 g/L sugars in the prehydrolyzate (30 g/L xylose) | Ref: 740, 160 °C, 28 %, 17.8 %<br>Extracted: 270, 28 %, 17.8 % | Ref: 54.7 % (13.1)<br>Extracted: 39.7 % (13.6) |
| Saukkonen et al. 2012b | Scots pine | $H_2SO_4$ at 0.5 wt-% on wood,150 °C, 35 min[5], 4.6:1, no washing[5] | 16.2 % | Ref: 1600, 160 °C, 35 %, 20 %<br>Extracted: 1250, 160 °C, 35 %, 22 % | Ref: 46.9 % (25.4)<br>Extracted: 39.5 % (27.2) |
| **Alkali extraction** | | | | | |
| Helmerius et al. 2010 | Birch | White liquor at EA 3 %, 160 °C, 60 min, 3:1, no washing | 9 %, with 3.62 g/L xylan in the extract | Ref: 500, 160 °C, 37 %, 21 %<br>Extracted: 486, 160 °C, 37 %, 18 % | Ref: 51.7 % (17.9)<br>Extracted: 50.5 % (16.7) |
| Wafa Al-Dajani and Tschirner 2008 | Aspen | 1.67 M NaOH solution, 90 °C, 240 min, 4:1, no washing | Total 19.3 % (recovered 11.0 %), of which 40 % carbohydrates (27 % xylan) | Ref: 614, 170 °C, 25 %, 21 %<br>Extracted: 461, 170 °C, 40 %, 12 % | Ref: 52.7 % (23.1)<br>Extracted: 53.3 % (23.3) |

| Extraction method and reference | Wood type | Extraction conditions (Extracting liquor[1], T, t, LTW[2], washing) | Extraction yield (on dry wood), composition of the extract | Pulping conditions (H-factor, Max T, sulfidity, EA[3]) | Yield on wood after cooking (kappa) |
|---|---|---|---|---|---|
| Mao et al. 2010 | Mixed northern hardwoods | Green liquor (TTA[6] ~1 %), 160 °C, 110 min, 4:1 | 9 %, of which 39 % fermentable sugars | Ref: 1350, 30 %, 19.4 %<br>Extracted: 600, EA 18.1 % | Ref: 48 % (17)<br>Extracted: 46 % (17) |

[1] If not water.
[2] Liquor-to-wood ratio
[3] Effective alkali, as NaOH.
[4] Two separate experiments of water prehydrolysis were carried out in the study. In the first one, carried out at 150 °C, the chips were washed after extraction and the amount and composition of the prehydrolyzate were evaluated. In the second, the extraction was carried out at a temperature of 160 °C but with the same prehydrolysis severity (the so-called P-factor (see Sixta et al. (2006) for a definition) was 200 in both experiments). After the second experiment, the chips were cooked after draining the reactor, with no intermediate washing.
[5] First heating up at 2 °C/min from 80 to 150 °C, then for 93 min (water prehydrolysis) or 35 min (acid prehydrolysis) at 150 °C. The extraction experiments were carried out twice, first with washing to evaluate the total amount of dissolved material. The extraction experiments followed by cooking were in turn carried out without intermediate washing.
[6] Total titratable alkali, wt-% on wood. Also 0.05 wt-% on wood of anthraquinone was added to the extraction liquor.

As can be seen in the table, the yields on wood after cooking (mass of brown stock pulp/mass of wood chips prior to extraction) decreased by approximately 5 to 17 percentage points in the reviewed water and acid-catalyzed prehydrolysis studies. Assuming constant pulp production, these decreases would correspond to wood consumption increases in the range of 10 % to 45 %. The decreased yield can be particularly attributed to increased overall (taking both hemicellulose extraction and cooking into account) dissolution of hemicelluloses. The acidic conditions in water prehydrolysis, resulting from the generation of acetic acid, hydrolyze and dissolve hemicelluloses partially. The hemicelluloses remaining in the wood chips are furthermore susceptible to dissolution in the alkaline cooking (see e.g. Bernardin 1958), resulting in a decrease in the yield on wood after cooking and a high cellulose content of the produced pulp (Wafa Al-Dajani et al. 2009). From the mass balance data over water prehydrolysis and kraft cooking of aspen published in the study of Wafa Al-Dajani et al. (2009), it can be calculated that approximately 50 % of the original xylan present in the wood chips was dissolved in water prehydrolysis, while the amount of xylan dissolved in cooking was in absolute terms (based on the same mass of original wood chips) relatively similar between the water prehydrolyzed and unhydrolyzed (control) chips (at approximately 40 % on the original xylan in the wood chips). The overall xylan yield (on the original xylan) decreased from almost 60 % of the unhydrolyzed chips to slightly above 10 % in the water prehydrolysis case. Contrary to hemicelluloses, cellulose degradation has generally been found fairly unaffected by water prehydrolysis, indicated by similar viscosities between control and water prehydrolyzed pulps (see e.g. Yoon and van Heiningen 2008; Saukkonen et al. 2012b). More severe conditions of acid-catalyzed prehydrolysis have in turn been found to result in increased overall cellulose degradation and decreased pulp viscosity (Mendes et al. 2009; Saukkonen et al. 2012b). Comparing the water and acid-catalyzed extraction experiments carried by Mendes et al. (2009) and Saukkonen et al. (2012b), it can furthermore be seen that acid-catalyzed prehydrolysis reduces the yield on wood more than water prehydrolysis. Compared to acid-catalyzed prehydrolysis, the advantage of water prehydrolysis is therefore its less severe conditions.

From most of the water and acid-catalyzed prehydrolysis studies reviewed in Table 4, it can be calculated that, in addition to decreased yields on wood, also digester yields (mass of brown stock pulp/mass of (pre-extracted) chips to digester) decreased. In some earlier studies (Amidon et al. 2006; VPP Project Final Report 2010), the digester yields of prehydrolyzed sugar maple (hardwood) chips were found to be higher than those of the control nonhydrolyzed chips. Such an increase for hardwoods was, however, not observed in the studies reviewed in Table 4, with the digester yields generally decreasing for both hardwoods and softwoods. In alkaline hemicellulose extraction, the yields on wood were similar to the reference (no extraction) while the digester yields were considerably higher. Galactoglucomannan, the dominant type of hemicellulose in softwoods is less stable in alkaline conditions than glucuronoxylan, the type of hemicelluloses dominant in hardwoods, and degrades easily by a peeling reaction. Hardwoods are therefore considered as more suitable raw materials for alkaline extraction methods (van Heiningen 2006).

In addition to the yield, hemicellulose extraction has a considerable effect on the conditions required in pulping to obtain a given lignin content in the pulp after cooking (characterized by a kappa number), decreasing the required cooking time (or cooking temperature) substantially. As can be seen in Table 4, most of the cooking experiments carried out with hemicellulose extracted chips required a lower H-factor than the reference cookings with no hemicellulose extraction. For example, for water prehydrolyzed chips, Wafa Al-Dajani et al. (2009) report an H-factor decrease of 460 (corresponding to a cooking time decrease of 35 %) and Helmerius et al. (2010) a decrease of 135 (13 % in cooking time). Improved delignification for water prehydrolyzed chips has also also been reported by Yoon and van Heiningen (2008), who calculated 40 – 60 % higher delignification rate constants than for the reference chips. The enhanced delignification of prehydrolyzed chips has been attributed to improved penetration of the cooking liquor due to an increased pore volume, resulting in better permeability of the cell wall, as well as hydrolytic cleavage of lignin structures and lignin-carbohydrate bonds during prehydrolysis (Sixta et al. 2006). As an alternative to a reduced cooking time or temperature, the conditions in cooking could also be adjusted by lowering the effective alkali (EA) level. By keeping the H-factor constant, Colodette et al. (2011) report on a decrease in the required EA level from 15.9 % for the reference, unhydrolyzed hardwood chips, to 15.4 % for prehydrolyzed hardwood chips to obtain a target kappa number of 17. EA reductions have also been studied by Wafa Al-Dajani et al. (2009) (hardwood, note that the EA was decreased in a cooking experiment that was different from the one listed in Table 4) and Yoon and van Heiningen (2008) (softwood). Similarly to water prehydrolysis, also the acid prehydrolysis and alkaline extraction studies presented in Table 4 resulted in a decreased H-factor or a lower EA level in cooking. At a constant kappa number after cooking of acid prehydrolyzed softwood chips, DeMartini et al. (2008) found a decrease in the effective alkali to increase the digester yield slightly. Decreasing the effective alkali is generally known to improve the cooking yield, with the effect being more pronounced with hardwoods than with softwoods (Sixta et al. 2006). It could therefore be assumed that the yield increase reported by DeMartini et al. (2008) for prehydrolyzed softwood chips woud be greater for hardwood chips.

Water prehydrolysis can generally be expected not to have a considerable effect on alkali consumption in cooking. With the same EA level in cooking, Yoon and van Heiningen (2008) (with the EA level for the reference cooking different from what is presented in Table 4) found the residual alkali level to be the same with the prehydrolyzed and reference softwood chips, indicating that water prehydrolysis did not have a significant effect on the alkali consumption. Mendes et al. (2009) found that a constant EA level in cooking resulted in a somewhat lower residual EA after the cooking of water prehydrolyzed hardwood chips than that of the reference hardwood chips, indicating a slight increase in alkali consumption. Also the data presented by Saukkonen et al. (2012b) for softwood raw material indicated a slight increase in alkali consumption. In alkaline extraction methods, alkali consumption in cooking of hemicellulose extracted chips is lower than with the reference chips (Wafa Al-Dajani and Tschirner 2008).

### Effects on the rest of the fiberline

In oxygen delignification, the hemicellulose content of the pulp can have an effect on both the degree of delignification and selectivity (Δviscosity/Δkappa). With a lower hemicellulose content, the efficiency of oxygen delignification (defined as the decrease in the kappa number) of pre-hydrolyzed pulps has been found to be higher than that of reference pulps (Sixta et al. 2006; Kautto et al. 2010b; Colodette et al. 2011). This improved response to oxygen delignification has been attributed to the lower hexenuronic acid (Hexa) content of prehydrolyzed pulps (Sixta et al. 2006; Colodette et al. 2011). As Hexa contributes to the measured kappa number but is not reactive against oxygen delignification, a lower relative Hexa content results in higher kappa number reduction (Sixta et al. 2006; Colodette et al. 2011). As the formation of Hexa is higher in hardwood than softwood cooking (Sixta et al. 2006), the effect of a lower HexA content can be expected to be more pronounced with prehydrolyzed hardwood pulps. Also the presence of other structures contributing to the kappa number, called non-lignin structures, being predominately derived from carbohydrate structures and not susceptible towards oxygen delignification, have been found to be less prevalent in prehydrolyzed pulps, contributing to their improved delignification (Sixta et al. 2006). The improved delignification of hemicellulose-poor chips is also in line with the findings of Zou et al. (2002), who varied the xylan content of pulp with the use of anthraquinone, and found that a higher xylan content led to a decreased rate of oxygen delignification. Although prehydrolysis increased the viscosity loss in oxygen delignification, both Kautto et al. (2010b) and Colodette et al. (2011) found the selectivity of prehydrolyzed pulps in oxygen delignification to be improved due to a more pronounced effect of the higher degree of delignification. Zou et al. (2002) found the higher hemicellulose content to increase selectivity.

In bleaching, the consumption of bleaching chemicals to obtain a given brightness level has been found to be lower for prehydrolyzed pulps than for reference pulps (Mendes et al. 2009; Kautto et al. 2010b; Colodette et al. 2011). This improved bleachability has been attributed to a lower kappa number after the $O_2$ stage, which in turn is due to a better response to $O_2$ delignification (Colodette et al. 2011). Also lower metal and Hexa contents (Mendes et al. 2009; Kautto et al. 2010b) could contribute to improved bleachability.

### Effects on chemical recovery

In water and acid prehydrolysis, the types of effects of hemicellulose extraction on chemical recovery are to a considerable extent dictated by the digester yield as well as the water and organic material carried over to cooking from the prehydrolysis stage. As the amount of the wood material extracted in prehydrolysis can have an effect on both the digester yield and the organic material carried over to cooking, the exact conditions applied in the prehydrolysis have an effect on the chemical recovery. Further, as discussed above, the water and acid prehydrolysis steps decrease the overall yield on wood after cooking quite significantly. This could result in either reduced pulp production (if wood consumption is assumed to be fixed), increased wood consumption (if pulp production is fixed) or a combination of these effects (if a decrease in yield is only partly compensated by increased wood consumption). The magnitude of the effects on the chemical recovery would depend considerably on which of these assumptions is adopted. The discussion below assumes that pulp production is kept fixed. The key aspects of a constant wood consumption scenario are then briefly discussed, followed by a discussion on alkali extraction methods.

The main effect of the prehydrolysis process can be seen in the evaporation plant and recovery boiler sections. Also the recaustizing plant and lime kiln can be affected. With the increased water content of prehydrolyzed chips, more water would end up in the evaporation plant, increasing the load on the plant (Frederick et al. 2008; DeMartini et al .2008; Hamaguchi et al. 2013). Furthermore, if prehydrolysis results in a decrease of digester yield, more wood chips would need to be fed to cooking, increasing the amount of generated black liquor and therefore the load on the evaporation plant (DeMartini et al. 2008).

The amount of organics dissolved in the black liquor could generally be expected to increase, with the exact degree of increase depending on the digester yield and the amount of recovered prehydrolyzate (and consequently on the amount of prehydrolyze entrained in the chips and carried over to cooking, increasing the organics content of the black liquor). Unless the chips are washed after prehydrolysis (which would enable a higher degree of prehydrolyzate recovery), the liquor-to-wood ratio in the prehydrolysis stage defines the amount of organics drained and recovered after the prehydrolysis. For pine wood chips, Kautto et al. (2010a) have estimated that 60 % of the organic material would be recovered with an LTW of 4. As discussed above, the digester yields of prehydrolyzed chips have generally been found to be lower than the yields of reference chips, increasing the amount of organic material dissolved in cooking (DeMartini et al. 2008). If not fully recovered, the amount of prehydrolyzate entrained in wood chip pores ends up in the black liquor, increasing the amount of dissolved organic material further. The increased organics content in the black liquor increases its heating value (DeMartini et al. 2008; Hamaguchi et al. 2013). Furthermore, with part of the hemicelluloses dissolved in prehydrolysis, less hemicelluloses are dissolved in cooking relative to lignin. As hemicelluloses (and hydroxy acids, their degradation products in alkaline pulping conditions) have a lower heating value than lignin (Vakkilainen 2000), the increasing lignin to hydroxy acids content in the black liquor increases the heating value further (DeMartini et al. 2008; Hamaguchi et al. 2013). With increased organic solids and heating value, the heat load on the recovery boiler would be increased, resulting in increased steam generation. As the prehydrolyzate is a relatively heterogenous mixture, various residues would result from its processing. Assuming that some of these residues would be evaporated along with the black liquor and combusted in the recovery boiler, the load on both the evaporation plant and recovery boiler would be increased further.

As discussed above, the load on the recovery boiler depends considerably on the digester yield and the amount of recovered prehydrolyzate. While the load on the recovery boiler is generally expected to increase, an increased digester yield of prehydrolyzed chips compared to reference chips, in combination with a high prehydrolyzate recovery rate can in principle result also in a decreased load on the recovery boiler (see the VPP Project Final Report (2010), where the water prehydrolysis of hardwood increased the digester yield, enabling an increase in pulp production with a constant load on the recovery boiler).

In the recausticizing plant and the lime kiln, the effects would depend both on the digester yield and alkali charge in cooking. With constant alkali charge on wood to the digester, a decrease in the digester yield would result in an increasing amount of (pre-extracted) wood chips fed to cooking. This would result in corresponding increase in the load on the recausticizing plant and the lime kiln load. As the digestibility of prehydrolyzed chips is better than that of reference chips, decreasing the effective alkali level in cooking could be an alternative to avoid capacity increases in the recausticizing plant and the lime kiln. (DeMartini et al. 2008)

As the effects on chemical recovery depend on the amount of extracted organic material, the digester yield and whether or not the wood chips are washed between prehydrolysis and cooking, varying degrees of effects have been reported in the literature. Frederick et al. (2008) studied the effect of acid prehydrolysis on the capacity utilization of different process sections in a softwood pulp mill. They apparently assumed a full recovery of the prehydrolyzate between prehydrolysis and cooking and varied the amount extracted wood material in the range of 6 – 18 %. For example, with 14 % of the wood material extracted, the digester yield decreased from the 46.6 % of the reference to 42.4 %, and load increases in the chemical recovery section for the evaporators, recovery boiler, recausticizing plant and lime kiln were found to increase by approximately 23%, 19%, 10%, and 10 %, respectively. With the capacity increase on the recovery boiler, the amount of excess power sold to the grid increased. Based on the material balances over water prehydrolysis and cooking presented in Publication I of this thesis (see subchapter 5.1), Hamaguchi et al. (2013) found the extraction of 14.1 % of wood material in the water prehydrolysis of softwood (with no washing between prehydrolysis and cooking), resulting in a slight increase in the digester yield, to result in a 16 % capacity increase in the evaporation plant, a steam generation increase of 13.5 % in the recovery boiler, and no significant effect on causticizing. Although the load increase on the evaporation plant increased steam consumption, the increased steam generation in the recovery boiler resulted in increased electricity production (Hamaguchi et al. 2013).

In a constant wood consumption scenario, a decreased yield on wood would result in decreased pulp production, not in increased wood consumption. Compared to constant pulp production, the amount of dissolved organics in the chemical recovery cycle would therefore be decreased. The exact amount of dissolved organics would depend on the amount of recovered prehydrolyzate (and consequently on the amount of the prehydrolyze entrained in the chips and carried over to cooking, which would depend on the LTW and whether or not the chips were washed after pre-extraction), as well as the digester yield. The decreased digester yields in most of the water and acid prehydrolysis studies presented in Table 4 would result in slight increases in dissolved organics with 60 % of the prehydrolyzate recovered (no washing), and decreases with full prehydrolyzate recovery. With part of the organic material extracted prior to cooking, less wood would be fed to cooking. With a constant effective alkali level on wood, the load on the recausticizing plant and the lime kiln would be reduced.

In alkaline extraction methods, including the near neutral extraction using green liquor (Mao et al. 2010), alkali solutions (Wafa Al-Dajani et al. 2008; Huang et al. 2010) and white liquor (Helmerius et al. 2010), the overall yields on wood after cooking are generally comparable with reference cooking and the digester yields are higher. With a constant pulp production, this could decrease the amount of organic material dissolved in the black liquor. With 10 % of wood material extracted in a near neutral green liquor extraction process and with washing between extraction and cooking, Lundberg et al. (2012) calculated a decrease in black liquor flow rate and organic content to decrease steam generation in recovery boiler by 12 %. With a decreased black liquor flow, the load on the evaporation plant could be slightly decreased (Lundberg et al. 2012). With an increasing digester yield, the amount of wood chips fed to cooking would be lower, decreasing the alkali charge. This, along with a possible decrease in the effective alkali level required in cooking, would result in off-loading of the lime kiln (Mao et al. 2010) and the recausticizing plant. Withdrawing green liquor from the chemical recovery cycle and using it in the hemicellulose extraction stage could, however, result in disruptions in the sodium sulfur balance of the mill (Lundberg et al. 2010).

### Effects on the properties of pulp

Concerning the properties of pulp, the main effects of hemicellulose extraction can be seen in the beating response and strength properties. Compared to unhydrolyzed pulps, water prehydrolyzed pulps have been found to require considerably more beating to obtain a given freeness (Yoon and van Heiningen 2008; Kautto et al. 2010b; Colodette et al. 2011), indicating decreased beatibility of prehydrolyzed pulps. This is in line with previous findings on the better beating response of higher hemicellulose content pulps (Young 1994). As hemicelluloses contribute to the swelling tendency of fibers, which in turn has an impact on the beating response, a lower hemicellulose content of prehydrolyzed pulps results in poorer beatability. Unlike water prehydrolyzed pulps, Walton et al. (2010) found green liquor -extracted pulps, which have a hemicellulose content similar to reference pulps, to respond to beating in a relatively similar way as reference pulps. In addition to beatability, the hemicellulose content has an effect also on numerous other fiber properties. Decreased hemicellulose content generally results in decreased water retention, increased hornification, and an increased tendency for fiber deformation and damage (Saukkonen 2014).

Concerning the strength properties, a decrease in the hemicellulose content of pulp has generally been attributed to a decrease in the tensile index and an increase in the tear index (Molin and Teder 2002). While all studies on water phehydrolyzed pulps have reported a decrease in tensile strength, increased tear strength has been found in several studies at a given degree of beating (see e.g. Annergren et al. 1963; Yoon and van Heiningen 2008; Helmerius et al. 2010). Colodette et al. (2011) in turn report a decrease in tear strength with beaten water prehydrolyzed pulp, while Duarte et al. (2011) and Saukkonen et al. (2012b) report of decreased tear strength with unbeaten pulps. As a decreased hemicellulose content is associated with decreased fiber-to-fiber bonding, which in turn is known to increase tear strength and decrease tensile strength, changes in the strength properties of paper made from hemicellulose-poor pulps have been attributed to reduced fiber-to-fiber bonding (Kautto et al. 2010b; Saukkonen 2014). A decreased fiber-to-fiber bonding is further associated with decreased brittleness and an increased light-scattering coefficient and opacity (Saukkonen 2014). With alkali-extracted pulps, the effects on strength properties can be expected to be lower than with water prehydrolyzed chips (Helmerius et al. 2010).

### Summary of the effects on pulp mill operation

As discussed above, the extraction of hemicelluloses prior to kraft pulping has an effect on both the operation of the pulp mill and the quality of the pulp. Table 5 below summarizes the key effects.

Table 5: Summary of the effects of water prehydrolysis on fiberline, chemical recovery and pulp quality. The effects on fiberline and chemical recovery are based on a constant pulp production scenario. Concerning fiberline and chemical recovery, the summary is based on the literature review presented above. The pulp quality part is based on Saukkonen (2014).

| Property | Effect of water prehydrolysis[1] | Comment |
|---|---|---|
| **Fiberline** | | |
| Yield on wood | Decreases | In the studies reviewed in Table 4, the yield on wood decreased by 5 to 17 percentage points. In a constant pulp production scenario, this corresponds to a wood consumption increase (and consecutive load increase on the upstream equipment) of 10 % to 45 % |
| Digester yield | Varies but generally appears to decrease | For most of the studies reviewed in Table 4, the digester yields decreased somewhat. Along with the extent of prehydrolyzate recovery, digester yield defines the increase in the amount of dissolved organics entering chemical recovery |
| Required H-factor in cooking | Decreases | To obtain a given kappa number, prehydrolyzed chips require shorter cooking (or lower temperature) than reference (unhydrolyzed) chips. Alternatively to a reduced H-factor, prehydrolyzed chips can also be cooked with a reduced EA level. |
| Response to $O_2$ delignification | Increases | Prehydrolysis increases the degree of delignification in $O_2$ delignification |
| Response to bleaching | Increases | To obtain a given brightness level, prehydrolyzed pulps require a lower amount of bleaching chemicals than reference pulps |
| **Chemical recovery** | | |
| Load on the evaporation plant | Increases | Prehydrolysis increases the water content of chips fed to cooking, increasing the load on evaporation. A decreased digester yield, which would result in increased wood chip feed and consecutively black liquor generation, would increase the load further. |
| Load on the recovery boiler | Increases | Due to entrainment of prehydrolyzate in the chips fed to cooking, a potentially decreased digester yield and increased lignin content of black liquor, the load on the recovery boiler increases. A possible combustion of prehydrolyzate residues in the recovery boiler would increase the load further. |

| | | |
|---|---|---|
| Recausticizing and lime kiln | Varies but generally appears to increase | With a constant alkali charge on wood in cooking, a (potentially) decreased digester yield would increase the wood chip feed to cooking and therefore load on the recausticizing plant and the lime kiln. |
| **Pulp quality** | | |
| Beating response | Decreases | A decreased hemicellulose content reduces the swelling tendency of fibers, which decreases fibrillation during beating, and thereby makes the beating response poorer. The swelling tendency of hemicelluloses can be contributed to their strong water-binding ability, which also explains the decreased water retention of hemicellulose-poor pulps. |
| Fiber-to-fiber bonding | Decreases | Hemicelluloses contribute to bonding between fibers. A decreased hemicellulose content therefore decreases inter-fiber-bonding, which has an effect on several paper properties (including strength and optical properties). |
| Tensile strength | Decreases | Decreased fiber-to-fiber bonding contributes to decreased tensile strength |
| Tear strength | Increases | Decreased fiber-to-fiber bonding contributes to a change in the tearing mechanism of paper, improving tear strength |
| Opacity and light scattering | Increases | Decreased fiber-to-fiber bonding contributes to increased light scattering and opacity |

[1] Water prehydrolysis decreases the hemicellulose content of the produced pulp. The effects of water prehydrolysis on pulp quality are discussed from the point of view of general decrease in the hemicellulose content.

### 3.1.3 Composition of the hemicellulose containining stream and its processing to ethanol

The exact composition of the hemicellulose-containing extraction liquor depends on the conditions applied in the extraction and the type of wood material. In the studies reviewed in Table 6 below, the carbohydrate content in the liquor varied from approximately 40 % to 80 %. In auto- and acid -catalyzed prehydrolysis processes, the prehydrolyzate is acidic. In the auto-catalyzed (water) prehydrolysis, this is due to the acetic acid liberated from the acetyl groups of the xylan backbone. The pH depends on the applied conditions (time and temperature) and is typically in the range of 3 – 5 (Wafa Al-Dajani et al. 2009; Colodette et al. 2011; Helmerius et al. 2011). In acid-catalyzed prehydrolysis, the pH is lower, being typically in the range of 1 – 2 (Wafa Al-Dajani et al. 2009). In auto-catalyzed prehydrolysis, the carbohydrates dissolved in the prehydrolyzate are typically to a considerable degree present in oligomeric or polymeric form (Yoon et al. 2008; Leschinsky et al. 2009), whereas acid-catalyzed prehydrolyzates have a higher content of monomeric sugars (Mendes et al. 2009). The oligomeric and polymeric carbohydrates of the prehydrolyzate from auto-catalyzed prehydrolysis can be converted to monomeric sugars in a separate post-hydrolysis step catalyzed either by dilute acid or enzymes (Carvalheiro et al. 2008). As the dominant type of hemicellulose in hardwoods is glucuronoxylan, hardwood prehydrolyzates contain predominately xylose. Xylose is a five-carbon monomeric sugar (pentose). Softwood prehydrolyzates, in turn, contain considerable amounts of six carbon hexose sugars (hexoses). In addition to carbohydrates and acetic acid, the prehydrolyzate can contain insoluble and soluble lignin fractions, extractives, ash, and various compounds originating from carbohydrates (such as furfural and hydroxymethylfurfural, degradation products of C5 and C6 sugars, respectively) (Wafa Al-Dajani et al. 2009; Leschinsky et al. 2009; Yoon et al. 2008; Frederick et al. 2008). Several of these compounds are potential inhibitors to the fermenting microorganisms (Frederick et al. 2008; Lehto and Alén 2015). Various conditioning steps may therefore be needed before the prehydrolyzate can be fermented to ethanol.

In addition to the inhibitory effects of some of the components present in the prehydrolyzate, another challenge in the processing of the prehydrolyzate is the tendency of the lignin liberated in the prehydrolysis to form sticky precipitates. The processability problems caused by these precipitates has been a considerable impediment to applying water prehydrolysis in the liquid phase and recovering and further processing of the prehydrolyzate (Leschinsky et al. 2007, 2008, 2009; Sixta et al. 2013). Adsorption of lignin on activated charcoal in high temperature immediately after prehydrolysis has been recently suggested as one method to reduce the formation of precipitates (Gütsch and Sixta 2011).

The processing of prehydrolyzate (or also the hemicellulose-containing liquor after green liquor extraction) to ethanol is often first assumed to include flashing (Frederick et al. 2008; Mao et al. 2010). If the carbohydrates are primarily in the form of oligomers (such as after water prehydrolysis or green liquor extraction), flashing is typically followed by post hydrolysis (Mao et al. 2010) to produce monomeric sugars. Lime is then used to neutralize the liquor and precipitate the sulfuric acid used in post hydrolysis as gypsum. The neutralized liquor is fermented to ethanol, followed by the recovery and purification of ethanol by distillation and molecular sieves (Frederick et al. 2008; Mao et al. 2010). As the prehydrolyzate is a very heterogeneous mixture containing numerous inhibitors and other components and as also various other products than ethanol can in principle be produced or separated from the prehydrolyzate, numerous other processing steps have been studied, including solvent extraction, precipitation, chromatographic separation, ion exchange, and activated charcoal and membrane filtration (Lehto and Alén 2015).

In addition to the abovementioned issues with sticky precipitates, inhibitory compounds and the heterogeneous nature of the prehydrolyzate in general, the prehydrolyzate is typically also very dilute. It contains carbohydrates in very low concentrations which makes its processing costly. Particularly with hardwoods, a large fraction of the extracted carbohydrates are furthermore pentosans (especially xylan) and their monomeric sugars, pentoses (C5 sugars, especially xylose). The fermentation of pentoses has traditionally been more challenging than the fermentation of hexoses (Lehto and Alén 2015).

In addition to the yield in fermentation (and, particularly in the case of hardwoods, the microorganism's ability to ferment C5 sugars), the ethanol output depends generally on the amount of carbohydrates dissolved in prehydrolysis as well as the amount of prehydrolyzate recovered from the prehydrolysis reactor. Table 6 reviews studies that have evaluated the potential ethanol output based on hemicellulose extraction.

Table 6: Review of simulation studies evaluating the simultaneous production of paper-grade pulp and ethanol based on hemicellulose extraction.

| Reference | Extraction method and wood type | Extraction & fermentation (amount[1] and composition in extraction, washing[2]/no washing, conversion rates of C5 and C6 sugars in fermentation) | Pulp output[3] | Ethanol output[3] (absolute & relative) |
|---|---|---|---|---|
| Frederick et al. 2008 | Acid prehydrolysis of loblolly pine | 14 %, with carbohydrate content 70 – 80 %, apparently full recovery of prehydrolyzate, conversion 85 % for C5 and 92 % for C6 sugars | 1268 t/d | 156 t/d (~12 % of pulp production) |
| Kautto et al. 2010a | Water prehydrolysis of scots pine | 14.1 %, with carbohydrate content 48 %, no washing, 90 % conversion for C5 and C6 sugars | 1000 Adt/d | 40 t/d (4 %) |
| Mao et al. 2010 | Green liquor extraction of mixed northern hardwoods | 9 %, with 39 % fermentable sugars, apparently washing, 90 % conversion for C5 and C6 sugars | 1 000 t/d | 32 t/d (3 % of pulp production), acetic acid output 50 t/d |
| Huang et al. 2010 | Alkali extraction of aspen | 11 %, with 40 % carbohydrates, no washing, 95 % conversion for glucose and 85 % for hemicellulosic sugars (based on Aden et al. 2002) | 1200 Adt/d[4] | 38 t/a (3 % of pulp production) |

[1] Amount of extracted wood material as a wt-% on dry wood

[2] Indicating that full recovery of extracted material was assumed in the study

[3] When the production outputs were reported on a annual basis and no information was available on mill availability, the outputs were converted to a daily basis, assuming plant availability of 350 d/a.

[4] Calculated on the basis of wood chip feed of 2000 bone dry t/d and pulp yield of 54 %

As can be seen in the table, the ethanol production potential is rather limited, being in the range of 3 – 4 % relative to pulp production in most of the reviewed studies. This could be considered as an additional drawback of the hemicellulose extraction process for the production of second generation ethanol, particularly in smaller pulp mills.

### 3.1.4 Techno-economic analyses of hemicellulose extraction combined with pulp production

Various techno-economic assessments have been carried out to evaluate the attractiveness of hemicellulose extraction, covering different extraction methods (water, green liquor and alkali) and products (ethanol and others). As particularly water and dilute acid prehydrolyses have a considerable effect on the yield on wood after cooking, and therefore either on wood consumption (constant pulp production scenario) or pulp production (constant wood consumption scenario), the assumed prices of wood, pulp and ethanol can have a considerable effect on the economics of hemicellulose extraction. The main focus in this thesis is on water prehydrolysis for the co-production of paper-grade pulp and ethanol. As the dilute acid prehydrolysis has rather similar effects on the yield, this subchapter summarizes briefly a number of water and dilute acid studies. The studies will be discussed on a general level, not reviewing in detail e.g. the price levels and the assumptions adopted in hemicellulose extraction and its processing as well as the effects of extraction on pulp mill operation.

Published studies closest to the focus of this thesis can be considered to be the study of Frederick et al. (2008) and the final report of VPP (Value Prior to Pulping) project (VPP Project Final Report 2010). Frederick et al. (2008) evaluated the dilute acid prehydrolysis of loblolly pine for the co-production of paper-grade pulp and ethanol. Although the relative ethanol output was found to be high (see Table 6 above), the economics of the concept were generally found to be unattractive. Ethanol co-produced from the extracted hemicelluloses in combination with pulp production resulted in higher production cost than the production of ethanol only from all the carbohydrates present in loblolly pine (in other words, no pulp production). This was largely due to the considerable yield decrease in pulping. The capital cost per unit of produced ethanol was also found to be high, due to e.g. the small scale of ethanol production. The amount of ethanol produced depended on the amount of extracted wood material. As presented in Table 6, extracting 14 % of wood material in a plant producing 1268 t/d of brownstock pulp (427 kt/a), the ethanol production was 156 t/d (53 kt/a, 66 million liters/a). The capital investments of the hemicellulose extraction and ethanol production processes as well as the required pulp mill modifications were calculated to total 279 MUSD (Frederick et al. 2008).

Water prehydrolysis was studied In the VPP project (VPP Project Final Report 2010). Also this study found the hemicellulose extraction concept for a softwood (pine) to be economically infeasible. As mentioned above in subchapter 3.1.2, with hardwood (maple) chips the digester yield was found to be higher than with reference (no extraction) chips. The results were therefore somewhat more promising for hardwood. In the so-called optimum extraction conditions, with approximately 8 % of the wood material extracted in water prehydrolysis, a constant pulp production scenario (1398 t/d of pulp, approximately 480 kt/a), production of 19 kt/a of ethanol (25 million liters/a) and 6 kt/a of acetic acid, the extraction was found to be relatively unattractive. A so-called constant recovery scenario reached in turn modest profitability (8 % internal rate of return, IRR). In this scenario, pulp production was increased by 6 % (from 1398 t/d to 1476 t/d, which resulted in a corresponding increase in ethanol and acetic acid output), while maintaining the load on the recovery boiler at its reference level. This increased pulp production appears to have contributed substantially to the improved profitability of the concept. The increased pulp production was enabled by a considerably increased digester yield (52.7 % for the prehydrolyzed chips, 50.9 % for the reference), which reduced the amount of organics dissolved in the black liquor. The study appeared to assume a full recovery of the prehydrolyzate. A partial entrainment of the prehydrolyzate would have increased the organics load and reduced or eliminated the opportunities to increase pulp production. The investment costs for the hemicellulose extraction, as well as the ethanol and acetic acid production processes totaled 101 and 106 MUSD for the constant pulp and constant recovery scenarios, respectively.

In addition to the two studies described above, also other studies have been done on the economics related to water prehydrolysis. Hörhammer et al. (2014) studied the co-production of lactic acid and pulp in a water prehydrolysis-based biorefinery utilizing larch as a feedstock. Polysulfide and anthraquinone were added into the cooking of prehydrolyzed chips. By comparing this to the reference kraft process, they found the payback time of the investment into the extraction and co-product manufacture to be short. Jansson et al. (2014) studied the economics of converting a prehydrolyzate derived from water prehydrolysis of spruce into an oxygen barrier film. Instead of paper-grade pulp (which is the focus of this thesis), the prehydrolyzed chips were used in the production of dissolving pulp. By comparing to a reference case where the prehydrolyzate was evaporated and combusted in the recovery boiler, they found the conversion of the prehydrolyzate to be moderately promising (return on investment 8 %) when an upgraded prehydrolyzate (which would then be converted to the barrier material) was valued at 500 EUR/t. Unsurprisingly, the economics of the process were very sensitive to the assumed value of this intermediate stream.

In addition to water and dilute acid prehydrolysis, also the economics of green liquor (Mao et al. 2010, see also Tables 4 and 6) and alkali extraction have been studied (Huang et al. 2010, see also Table 6).

## 3.2 Organosolv pulping

### 3.2.1 Background and introduction

In organosolv pulping, pulping is carried out in the presence of an organic solvent. Lignin is cleaved during pulping and dissolved in the solvent (McDonough 1993). The development of organosolv pulping technologies was initiated by the work of Kleinert and Tayenthal (1931, 1932), who found in the 1930s that mixtures of ethanol and water at an elevated temperature and pressure could be used to pulp wood (Kleinert and Tayenthal 1931, 1932; Hergert 1998). Subsequent work on organosolv pulping established that various solvent systems with or without acidic catalysts could be used. The produced pulp was generally intended to be used as paper-grade pulp in the production of paper. During the first decades of the development of organosolv pulping, the process was, however, generally considered as unattractive due to the cost of the solvent, and no clear advantage in pulp yield or quality over the conventional processes (especially kraft pulping) (Hergert 1998).

With more stringent environmental and safety regulations in the 1970s, organosolv pulping, which did not have especially the odour problems associated with sulfuric compounds and the potential smelt explosions of kraft recovery boilers, gained renewed interest within the forest industry. Further, with the oil crises in the 1970s, organosolv pulping started to receive interest as a delignification (pretreatment) step prior to enzymatic saccharification of woody material for ethanol production. With the disappearance of the oil crises, organosolv pulping was again considered primarily as an environmentally friendly method for paper-grade pulp production (Hergert 1998). In addition to environmental benefits, with the lower capital expenditure expected for the organosolv process than the kraft process, the organosolv process was considered more suitable for small-scale operation (Hergert 1998; Aziz and Sarkanen 1989). Furthermore, organosolv pulping enabled the recovery of valuable by-products, especially lignin (Aziz and Sarkanen 1989). A number of organosolv processes for pulp production had undergone major development activity in pilot or larger scale by the mid-1990s. These processes were ALCELL (ethanol-water), ASAM (alkali-sulfite-anthraquinone-methanol), MILOX (formic acid-performic acid), and Organocell (the process was initially piloted as a two-stage system, but a larger mill was based on only one pulping stage, in two stages: methanol-water (first stage) and NaOH-methanol-water (second stage), in one stage: methanol-water-NaOH-anthraquinone) process (Hergert 1998).

Currently there are no known full-scale organosolv plants in operation. Along with the general interest in the production of lignocellulosic ethanol, the focus in organosolv development (especially with ethanol-water based systems) has shifted from pulp production towards the use of organosolv pulping as a pretreatment step in bioethanol production (Pan et al. 2005, 2006). Within pulp production, organosolv pulping has recently been considered especially for the pulping of non-wood feedstocks (Leponiemi 2008).

### 3.2.2 Solvent systems and process concepts

A wide range of organic solvents has been examined as pulping agents for organosolv cooking, including alcohols (such as methanol and ethanol), organic acids (such as formic acid and acetic acid), ethyl acetate, phenol, and dioxane (Hergert 1998; Muurinen 2000). Furthermore, pulping can be carried out either in acidic or alkaline conditions. Using neutral solvents, the acidic conditions in pulping are either a result of acetic acid cleaved from hemicellulose acetyl groups during pulping, or an acid can be used as an additional catalyst. Alternatively, pulping can be carried out with acidic solvents. In alkaline organosolv systems, organic solvents are used in combination with alkali.

In acidic organosolv pulping, lignin is fragmented and dissolved in the organic solvent (McDonough 1993), with the main pathways of lignin breakdown being acid-catalyzed cleavage of β-O-4 linkages and ester bonds (Sannigrahi et al. 2010). Carbohydrates, in turn, undergo hydrolysis reactions, dissolving partially in the cooking liquor as oligomeric and monomeric sugars, which can possibly react further to sugar degradation products. After pulping, the dissolved lignin can be precipitated from the pulping liquor by dilution with water (Lora and Glasser 2002).

Alkaline organosolv pulping processes include the ASAM and Organocell processes described briefly in the previous subchapter. The reactions taking place in alkaline conditions in the cooking stage can be expected to be relatively similar whether or not a nonaqueous (organic) solvent is added into the cooking liquor (McDonough 1993). The possible recovery of lignin is carried out by first recovering the organic solvent from the cooking liquor, followed by precipitation from the aqueous alkaline liquor by neutralization. Compared to acidic conditions, the structure of the lignin recovered from alkaline organosolv pulping can be considerably more changed. Furthermore, as soluble carbohydrates are converted to aliphatic and hydroxyl carboxylic acids (similar to the reactions taking place in soda and kraft pulping) (Hergert 1998), recovery of soluble carbohydrates is not possible. Alkaline pulping processes would also require a more complex recovery of pulping agents than acidic processes, with the recovery and regeneration of alkali requiring a recovery furnace and recausticizing plant. For these reasons, alkaline organosolv processes have been envisioned mainly solely for pulp production (Hergert 1998), and primarily acidic organosolv concepts have been considered also as pretreatment and fractionation methods for ethanol generation. The focus in this chapter is therefore specifically on acidic systems.

One of the acidic organosolv systems with most current interest as a pretreatment method prior to enzymatic hydrolysis is ethanol-based pulping. The ALCELL process, a non-catalyzed ethanol pulping process, was developed by Repap Enterprises in the 1980s for the development of paper-grade pulp. A demonstration-scale plant located in New Brunswick, Canada, was operated intermittently from 1989 to 1996. The organosolv technology was later acquired by Lignol Innovations Corporation. Instead of producing pulp, Lignol aimed at commercializing the technology as an ethanol producing biorefinery (Pye 2010a). Lignol started production in a pilot plant in 2009 (Lignol 2009) (note: the company went into receivership in 2014 (Lignol 2014), and was then acquired by Fibria (Fibria 2016)). Another company developing ethanol-based biorefinery is American Process with their AVAP (American Value Added Pulping) technology that uses ethanol and sulfur dioxide as pulping agents (Pylkkanen and Retsina 2006; AVAPCO 2014). The company has operated a demonstration facility since 2013 (AVAPCO 2014). In addition to pilot and demonstration scale operations aiming at commercial deployment of the technology, ethanol-based organosolv pretreatment has been studied widely in recent scientific literature, especially with sulfuric acid as a catalyst (see e.g. Pan et al. 2005, 2006; Sannigrahi et al. 2010; Cateto 2011). Also other types of solvent systems are currently under development. Chempolis and CIMV (Leponiemi 2011) are developing formic and acetic acid-based organosolv pulping processes, and have recently built pilot or demonstration -scale facilities (Chempolis 2009; CIMV 2014a). These companies aim specifically at processing non-wood feedstocks, either to cellulose pulp or alternatively further to sugars that can be used for the production of fuels and chemicals (Chempolis 2014; CIMV 2014b; CIMV 2014c). Leaf Resources is developing a glycerol-based biomass fractionation technology (Leaf Resources 2017).

The overall process concept for organosolv pulping and solvent recovery depends considerably on the selected solvent system. In an ethanol-based pulping process, the exact cooking conditions can vary. The temperature can be expected to be in the range of 185 – 198 °C and the ethanol concentration between 35 and 70 wt-% (Arato et al. 2005). The cooking can be either autocatalyzed or a mineral acid can be used as an added catalyst. The spent liquor from cooking is generally assumed to be flashed for partial recovery of the solvent and heat. The liquor is then diluted with water to enable the precipation and recovery of lignin. After lignin separation, the liquor is distilled to recycle the solvent back to cooking. Furfural can be recovered as a side-draw in the distillation column. The aqueous bottoms stream from the distillation, containing the hemicellulosic carbohydrates dissolved in cooking, is then concentrated by evaporation. Forming a tarry organic phase upon concentration, lower molecular weight lignin can be separated from the stream (Agar et al. 1998). Also extractives can be potentially separated from the aqueous stream during the evaporation stage (Pye and Rushton 2013), and acetic acid can be separated from the evaporation condensates (Hergert 1998; Pye and Rushton 2013). A schematic representation of a Lignol process concept is presented in Figure 6 below (based on Pye and Rushton 2013).

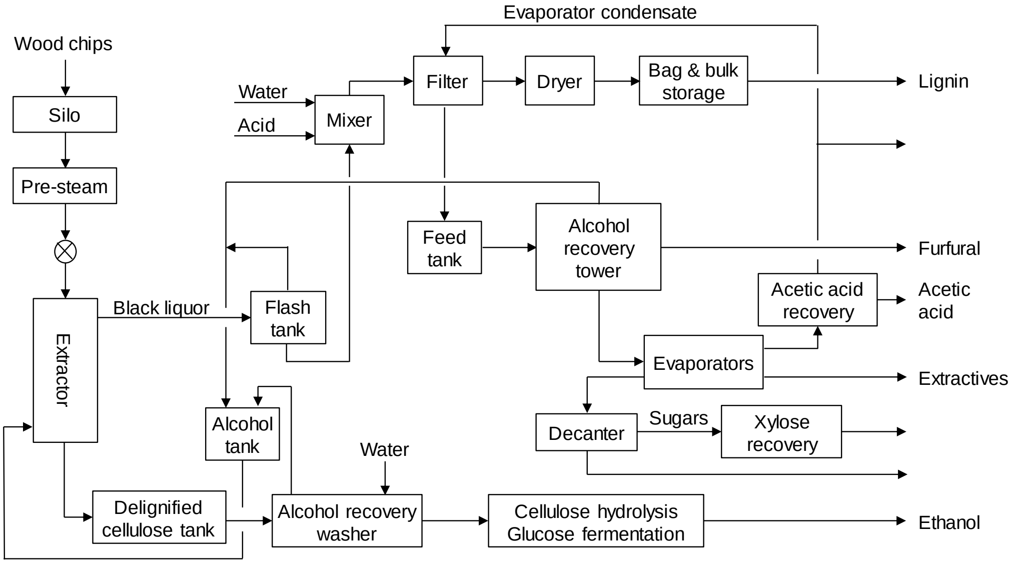


Figure 6: Schematic representation of a Lignol-type ethanol-based organosolv pulping process (based on Pye and Rushton 2013).

### 3.2.3 Utilization of fractionated product streams

As can be seen in Figure 6, organosolv pulping fractionates lignocellulosic biomass into three main fractions, cellulose pulp, lignin and aqueous stream containing primarily hemicelluloses. The conversion of these fractions into various products is discussed in this subchapter. In addition to these three main fractions, the organosolv biorefinery process enables the recovery of smaller volume co-products, including furfural and acetic acid (see the previous subchapter).

As discussed in subchapter 3.2.1, organosolv pulping was traditionally intended as a process for the production of paper-grade pulp. In papermaking applications, the properties of organosolv pulps have generally been described to be rather close to those of sulphite pulps (Young 1994). In addition to papermaking, the solid cellulose fraction could be used in the production of dissolving pulp or other cellulose products (Pye and Rushton 2013). An alternative approach for the processing of the cellulose fraction is its conversion to glucose monomers through enzymatic hydrolysis. The glucose monomers can then be fermented to ethanol (Pan et al. 2005, 2006). Fermentation or catalytic conversion of glucose to various other chemicals is also possible.

Organosolv lignin, separated from the spent cooking liquor by precipitation, has been described to be generally a lignin product of high purity, low molecular weight and narrow molecular weight distribution (Lora and Glasser 2002; Pye 2010a) that is sulfur-free and insoluble in water (Lora and Glasser 2002), as well as nonderivatized and reactive (Pye 2010a). Repap, operating the ALCELL demonstration plant from 1989 to 1996, reportedly sold organosolv lignin on a commercial basis to be used as a substitute for phenolic resins. Commercial applications for these resins were in the manufacture of oriented strand board (OSB) and friction materials (Pye 2010a). In addition to phenolic resins, also various other applications have been suggested for organosolv lignin, including epoxy resins and polyurethanes (Lora and Glasser 2002; Pye 2010b; CIMV 2014d).

After lignin separation and solvent recovery, the aqueous stream contains primarily hemicelluloses. The exact composition depends on the raw material, cooking conditions and processing after cooking, but can generally be expected to contain sugar monomers and oligomers (with hardwood as raw material, especially xylose and xylo-oligomers), as well as sugar degradation products and acetic acid (cleaved from hemicellulose acetyl groups). Similarly to the glucose produced through hydrolysis of the cellulose pulp, monomeric hemicellulose sugars can in principle be fermented to various chemicals, including ethanol. The fermentation of hemicellulosic sugars (being primarily pentose sugars containing five carbon atoms) has, however, been generally more challenging than the fermentation of glucose (hexose, six carbon atoms) (see e.g. Aden et al. 2002). Sugar degradation products present in the aqueous stream can furthermore inhibit fermentation. Besides the fermentation pathway, other possible pathways for the xylose-containing stream would include the production of furfural (Agar et al. 1998), xylitol (Arato et al. 2005) or biogas (Hallberg et al. 2011).

### 3.2.4 Simulation and techno-economic analyses of organosolv concepts

Several process design, process analysis and simulation studies on organosolv pulping processes have been presented in the literature. While a number of these studies have focused on the simulation of selected unit operations of organosolv process plants (García et al. 2011; Vila et al. 2003; Botello et al. 1999), also studies covering the whole process from pretreatment to ethanol production have been presented (Furlan et al. 2012; Ojeda et al. 2011; Kautto et al. 2013). Zhu and Pan (2011) and Ojeda et al. (2011) have compared the energy consumption in the production of sugars and ethanol, respectively, based on different pretreatment methods. Table 7 summarizes these technical studies.

Table 7: Process design and simulation studies on organosolv processes.

| Reference | Raw material and cooking solvent | Products produced in the process | Focus and findings |
|---|---|---|---|
| Kautto et al. 2013 | Hybrid poplar, ethanol-water with $H_2SO_4$ as a catalyst | Ethanol both from cellulosic and hemicellulosic sugars, lignin, furfural and acetic acid | Conceptual process design and simulation of an organosolv biorefinery producing ethanol and co-products. By comparing to a dilute acid pretreatment -based reference process, the organosolv process was found to have higher energy consumption and lower ethanol yield. |
| Furlan et al. 2012 | Sugarcane bagasse, ethanol-water (washing of the pulp with NaOH) | Ethanol both from cellulosic and hemicellulosic sugars, lignin combusted | Simulation of an integrated first (sugarcane juice) and second generation (bagasse) bioethanol production process. |
| Ojeda et al. 2011 | Sugarcane bagasse, ethanol-water, with $H_2SO_4$ as a catalyst | Ethanol both from cellulosic and hemicellulosic sugars | Simulation and energy and life cycle analyses on second generation bioethanol production based on different pretreatment methods. The organosolv process was found to result in high energy demand, resulting in highest life cycle emissions. |
| Zhu and Pan 2010 | Lodgepole pine, ethanol-water, with $H_2SO_4$ as a catalyst (based on Pan et al. 2008) | Cellulosic and hemicellulosic sugars | Energy analysis of different pretreatment methods. The energy consumption in organosolv pretreatment (not including solvent recovery) was generally found to be lower than in steam explosion and higher than in sulfite pretreatment to overcome lignocelluloses recalcitrance (SPORL). |
| García et al. 2011 | Lignocellulosic non-wood feedstock, ethanol-water | Cellulosic solid fraction (pulp), concentrated stream enriched in hemicellulosic sugars, lignin | Simulation and heat integration study of an ethanol-based organosolv pulping concept consisting of pulping, lignin and solvent recovery and washing of the cellulose pulp. |

| | | | |
|---|---|---|---|
| Vila et al. 2003 | Eucalyptus globulus, acetic acid-water, with HCl as a catalyst (acetosolv) | Cellulosic pulp, concentrated stream enriched in hemicellulosic sugars, lignin, furfural | Simulation study of acetosolv pulping, discussing the recovery of solvent, lignin, furfural, and hemicellulosic sugars in the process. |
| Botello et al. 1999 | Eucalyptus globulus, ethanol- and methanol-water | Cellulosic pulp, stream enriched in hemicellulosic sugars, lignin | Simulation study of the recovery of lignin, furfural, and solvent. |

Also studies covering the economic aspects of organosolv processing have been presented. Production cost (or minimum selling price) comparisons of ethanol production based on different pretreatment systems have been presented by Kautto et al. (2014), Dias et al. (2011) and Mabee et al. (2006). Dias et al. (2011) have also estimated the internal rate of return of ethanol production. Cost and profitability estimations for different organosolv processes have also been presented by Laure et al. (2014), van der Linden et al. (2012), Sundquist (1996) and Parajó and Santos (1995). González Alriols et al. (2010) have calculated the costs for organosolv lignin separated by ultrafiltration. Table 8 summarizes these techno-economic studies.

Table 8: Techno-economic studies on organosolv processes.

| Reference | Raw material and cooking solvent | Products produced in the process | Focus and findings |
|---|---|---|---|
| Kautto et al. 2014 | Hybrid poplar, ethanol-water with $H_2SO_4$ as a catalyst | Ethanol both from cellulosic and hemicellulosic sugars, lignin, furfural and acetic acid | Economic evaluation of an organosolv biorefinery producing ethanol and co-products. The organosolv process was compared to a dilute acid pretreatment -based reference process. The organosolv process was found to have a higher investment cost. With a basecase lignin price of 450 USD/t, it was further found to result in a higher minimum ethanol selling price (MESP) of 3.1 USD/gal (0.81 USD/L, 1030 USD/t) than the reference process (2.6 USD/gal, 0.69 USD/L, 870 USD/t). |
| Dias et al. 2011 | Sugarcane bagasse and trash, ethanol-water with different catalysts | Ethanol from cellulosic sugars, hemicellulosic sugars to biogas and combustion, lignin combusted | Simulation and economic analysis of integrated first (sugarcane juice) and second generation (bagasse and trash) bioethanol production processes based on different pretreatment methods. Organosolv pretreatment was found to result in ethanol output, investment and production cost and internal rate of return relatively similar to those of steam explosion. |
| Mabee et al. 2006 | Douglas fir, ethanol-water, with $H_2SO_4$ as a catalyst | Ethanol apparently both from cellulosic and hemicellulosic sugars, utilization of lignin not taken into account in base case cost analysis | Technical and cost comparison (costs presented on a relative basis) of ethanol production based on organosolv and sulfur dioxide-catalyzed steam explosion pretreatments, with organosolv found to result in lower costs. The sales price of lignin was further found to affect the production costs of the organosolv process significantly. |
| Laure et al. 2014 | Beech, ethanol-water with | Glucose, hemicellulosic (C5) sugars, organosolv | Pilot-scale experimental, simulation and economic assessment. The investment cost of a 400 kt dry |

| | | | |
|---|---|---|---|
| | $H_2SO_4$ as an optional catalyst | lignin and hydrolysis lignin | feedstock/a plant was 55 – 61 MEUR. The production cost of glucose was 218 – 257 EUR/t, with prices of C5 sugars and organosolv lignin of 200 EUR/t and 630 EUR/t, respectively. |
| van der Linden et al. 2012 | Various feedstocks, ethanol-water , with $H_2SO_4$ as a catalyst | Cellulose pulp, lignin and furfural (from hemicellulosic C5 sugars) | Economic evaluation. For a plant processing 150 kt feedstock/a, the total fixed capital was estimated at 80 to 87 million EUR. At pulp, lignin and furfural prices of 350, 750 and 625 EUR/t, respectively, the payback time was approximately 6 to 7 years. |
| Sundquist 1996 | Primarily birch, formic acid-performic acid (Milox) | Both paper-grade and dissolving pulp (lignin and hemicelluloses combusted) | Pilot-scale experimental and economic assessment. The properties of paper-grade pulp and investment cost of the Milox process were similar to those of kraft process, while the operating costs were higher due to a higher cost of energy and chemicals. |
| Parajó and Santos 1995 | Eucalyptus globulus, acetic acid-water, with HCl as a catalyst (acetosolv) | Cellulosic pulp, hemicellulosic sugars, lignin, furfural | Simulation and economic analysis. The process was clearly unprofitable at the fuel value of lignin, being closer to profitability with lignin priced as an asphalt extender and profitable at higher prices (priced e.g. as a phenol extender in phenol-formaldehyde resins). |
| González Alriols et al. (2010) | Miscanthus sinensis, ethanol-water | Cellulosic pulp, hemicellulose stream, lignin | Simulation, with ultrafiltration used to produce lignin fractions with varying molecular weights. The production cost of lignin was 52 EUR/t. |

From the simulation and techno-economic studies on organosolv pulping (Tables 7 and 8), it can be generally concluded that organosolv pulping is a relatively high energy consuming process due to solvent recovery (Ojeda et al. 2011; Kautto et al. 2013), and the price of organosolv lignin is an important factor in the economics of the process (Parajó and Santos 1995; Mabee et al. 2006; Kautto et al. 2014).

# 4 Research design

This chapter describes the methodological positioning of the research carried out in this thesis. The positioning is done on three levels, the philosophy of science, the research strategy and the research methodology. The specific methods applied in evaluating the two process concepts are also discussed.

## 4.1 Philosophy of science

The principal goal of science is to obtain and organize knowledge. Based on different understanding of the nature of knowledge and how it is to be obtained, various fields of science are often positioned on a continuum between two philosophies of science, positivism and hermeneutics (Olkkonen 1993).

Positivism, founded by Auguste Comte, is an empiristic school of thought (Olkkonen 1993; Arbnor and Bjerke 2009). The broader school of thought underlying it is realism (Olkkonen 1993). According to positivism, research and the generation of knowledge should be restricted to positive, empirically measurable facts. The aim of research is to describe phenomena and their causal linkages. Positivistic research should be objective and replicable, and the results verifiable. Positivistic research is typically quantitative, based on empirical data. Natural sciences rely solely on positivism (Olkkonen 1993).

Hermeneutics, originating from idealism, aims at interpreting and understanding the research subject (Olkkonen 1993; Arbnor and Bjerke 2009). As the research relies on the researcher’s understanding, it is more subjective by nature. The data is often qualitative and less generalizable than in positivism. However, the data often enables a deeper analysis of the research subject. The research is further generally less replicable and the results less verifiable than in positivistic research (Olkkonen 1993). Hermeneutics are considered to be of importance particularly in the field of humanities (Olkkonen 1993; Arbnor and Bjerke 2009).

In this continuum from positivistic to hermeneutic philosophies, technical sciences are normally positioned relatively close to positivism, while business research is located in the middle (Olkkonen 1993). The field of this thesis is industrial engineering and management. It draws heavily also from technical sciences, i.e. chemical engineering and pulp and paper technology, and is based to a considerable extent on empirical quantitative data. The research carried in this thesis can therefore be considered as mainly positivistic.

## 4.2 Research strategy

As a field, industrial engineering and management is applied science, aiming at both improving theoretical understanding and providing practical, useful information (Olkkonen 1993). There are, however, variations within the field in various terms, including the goals of the research (whether it aims more at a theoretical or a practical contribution), data (empirical or theoretical), as well as the philosophical basis (whether the research is inclined more towards positivism or hermeneutism). To classify research strategies along these lines, Neilimo and Näsi (1980) have introduced four general research strategies, the conceptual approach, the nomothetical approach, the decision-oriented approach, and the action-oriented approach. These were positioned on a framework with two dimensions: descriptive-normative and theoretical-empirical by Lukka (1991). Kasanen et al. (1991, 1993) have introduced a fifth, constructive approach and placed it in the framework.

The conceptual approach is descriptive (in other words, the research aims at answering questions such as “who is” and “why is”, and focuses on describing, explaining and forecasting), and theoretical (the research is based primarily on theoretical reasoning) (Lukka 1991). The aim of the conceptual approach is to develop new theoretical understanding of the research subject. It is based primarily on prior conceptual development and existing data and theories on the research subject. The research method contains typically analysis and synthesis (Olkkonen 1993). The nomothetical approach is empirical (based on empirically collected data (Lukka 1991)) and descriptive. With its background in positivism, it typically aims at establishing causality or at least correlation between some properties of the research sample by means of statistical analysis (Olkkonen 1993). The decision-oriented approach is theoretical and normative (goal-oriented research aiming at answering the question “how should we act” (Lukka 1991)). The decision-oriented approach aims at developing mathematical or computer-based models that are used in aiding decision-making. The research data consists typically of prior knowledge on interdependencies. These interdependencies are used to develop (e.g. simulation) models that describe the phenomenon being studied. The model is then used to e.g. solve a certain problem in a better way and to provide recommendations (Olkkonen 1993). The action-oriented approach is empirical, while on the descriptive-normative axis the approach is generally positioned in the middle. The approach draws strongly from hermeneutics, aiming at holistic understanding of a small number of research subjects (which could be e.g. the actions of organizations or leadership) (Olkkonen 1993). The constructive approach is empirical and normative. Similar to the decision-oriented approach, the constructive approach aims at developing problem-solving methods. Unlike the decision-oriented approach that relies on mathematical or computer models, the constructive approach relies on creativity, innovativeness and heuristics in problem solving (Olkkonen 1993).

As this thesis focuses strongly on the development of simulation models and the use of these models in drawing conclusions, the research approach can be considered to be the decision-oriented approach. Also the normativeness of the decision-oriented approach is visible in the thesis. By evaluating the feasibility of two biorefinery concepts, the thesis provides input for a potential decision by an actor active in this field to continue or stop the development of the concepts (“how should we act”). With the use of empirical data and heuristics, the thesis has also features of the other normative research strategy, the constructive approach.

## 4.3 Research methodology

In addition to the continuum between positivism and hermeneutism (see subchapter 4.1), another typical, and partly overlapping, way of positioning research is between deduction and induction. Deductive reasoning proceeds from general truths to more specific statements. It can be found primarily in theoretical research, where known, proven theories are used to deduce a new theory or conclusion concerning a subset or a specific case of the studied domain. Inductive reasoning, in turn, draws general statements from more specific facts. It is typical in empirical research where a group of specific cases is studied to draw conclusions that concern a wider population (Olkkonen 1993).

In this thesis, experimental laboratory and simulation work are used to study the two biorefinery concepts. In experimental laboratory work, the studied sample is assumed to represent the whole population, and the method is therefore inductive. Also simulation work has inductive characteristics. Specific data points (obtained from experimental work and literature) are used to develop simulation models which are assumed to represent larger entities, process concepts. Inductive reasoning is further used in drawing overall conclusions.

Also deductive reasoning is used throughout the work. General knowhow and literature of pulp and paper technology and processing of lignocellulosic feedstocks to second generation ethanol were used in the experimental work, the development of the simulation models, and drawing conclusions concerning the two studied processes (which can be considered as specific cases of the larger domain of pulp, paper and biorefinery technologies). While the simulation work was above described as having inductive features, it can also be considered as deductive. Various general theories (such as mass and energy conservation, thermodynamics) were used as the basis for building the specific simulation models. Work containing features of both inductive and deductive reasoning is often called abductive (Modell 2009; Järvensivu and Törnroos 2010). Both the simulation work and the thesis as a whole can therefore be considered as abductive.

As an abductive work, the thesis further contains features of critical realism (Modell 2009; Järvensivu and Törnroos 2010). Critical realism is an abductive research approach that does not assume, like pure positivism, that there is one universal truth that can be identified by objective observations. Rather, critical realism assumes that specific, local truths contingent with local conditions exist. It is possible to move closer to these truths through research (Järvensivu and Törnroos 2010). In this thesis, two biorefinery concepts are evaluated. As the development of lignocellulosic biorefinery concepts is still in an emerging stage, and optimal biorefinery design is always dependent on local, specific conditions (see further discussion in subchapter 6.5), no universal truths can be expected to be found. Critical realism can therefore be considered to be an applicable attitude concerning the expected outcomes of the thesis.

From the point of view of methodology, the thesis can also be considered as a case study, with the two studied process concepts being two specific cases. Eisenhardt (1989, p. 534) describes case study as a “research strategy which focuses on understanding the dynamics present within single settings”. The primary focus in this thesis is on understanding the studied process concepts, not the entire lignocellulosic biorefinery field. In a later article, Eisenhardt and Graebner (2007) describe case study as theory-building (inductive). As described above, this work contains inductive reasoning to a considerable extent. The study can therefore be well considered as a case study.

## 4.4 Methodological positioning of the study

As described above in subchapters 4.1 – 4.3, from the perspective of the philosophy of science, this work is inclined more towards positivism than hermeneutism. The research strategy was described to have features of particularly the decision oriented approach. The thesis was further characterized as abductive, having characteristics of both inductive and deductive reasoning. Due to the abductive character of the thesis, and due to the underlying assumption that the evaluation of biorefinery concepts is always contingent with local conditions, indicating that no ultimate truths concerning biorefinery designs can be found, the thesis was also argued to contain features of critical realism. Figure 7 below presents the methodological positioning of the thesis from these perspectives. It should be noted that in addition to critical realism, this thesis can also be described as a case study. The specific methods applied within the studied cases (process concepts) included experimental laboratory work and simulation. These are described in more detail in the following subchapter.

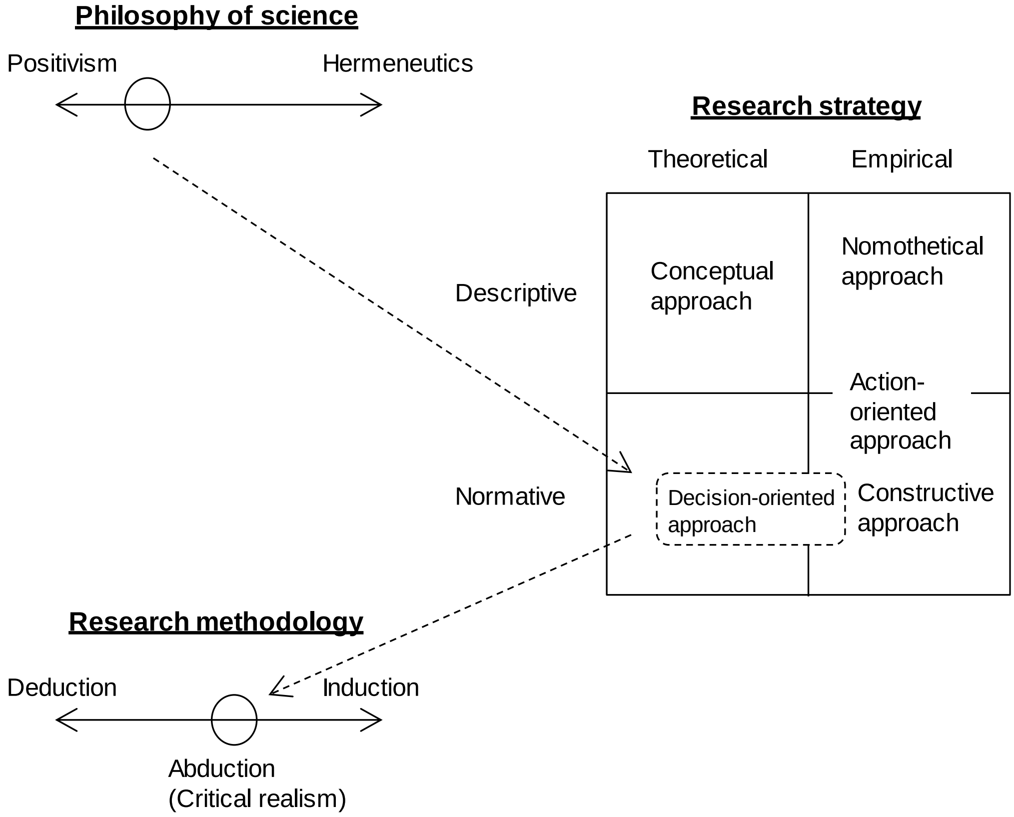


Figure 7: Methodological positioning of the thesis. The research strategy framework is based on Neilimo and Näsi (1980), Kasanen et al. (1991, 1993) and Lukka (1991).

## 4.5 Specific methods applied within the studied two process concepts

The work carried out in this thesis included experimental laboratory work and the development of simulation models. These were used to evaluate the two process concepts, hemicellulose extraction before kraft pulping and organosolv pulping. Subchapter 1.2. positioned the thesis in the lifecycle of a chemical product and process design in the concept stage. This subchapter presents an overview of the specific methods adopted in this thesis for the concept stage evaluation of the two process concepts. The methods are discussed separately for the two process concepts. The methods are described also in Publications I – IV.

### 4.5.1 Hemicellulose extraction before kraft pulping (Publications I and II)

Both laboratory and simulation work were carried out in evaluating the hemicellulose extraction process concept. The laboratory work included hemicellulose extraction experiments and the cooking of prehydrolyzed chips (Publications I and II), as well as bleaching and refining of prehydrolyzed pulps and testing of handsheets prepared from the prehydrolyzed pulps (Publication II).

#### Publication I

The objective of Publication I was to develop a simulation model over a pulp- and ethanol-producing pulp mill biorefinery based on hemicellulose extraction. The simulation model was based on both laboratory work and literature data. Since the laboratory work was used as the background data and basis for the simulation model, both the methodology and findings of the experimental work are reviewed in this subchapter. Also the development of the simulation model is described in this section. The actual findings of the publication (the outcome of the simulation work) are reviewed in subchapter 5.1.

The composition and amount of prehydrolyzate generated in water prehydrolysis were evaluated in experiments carried out at the University of Jyväskylä. The extractions were carried out in a 2 L reactor using screened (7 – 13 mm) pine wood chips. The liquor-to-wood ratio in the experiments was 5, and the extraction temperature was 150 °C. The extracted chips were washed after extraction. By varying the extraction time, the experiments were done at varying P-factor levels. Table 9 below presents the findings of the experiments.

Table 9: Chemical composition of the prehydrolyzate (as weight-% of original wood dry solids) from water prehydrolysis of pine wood chips at different P-factors (adapted from Kautto et al. 2010a, based on Rintaniemi 2009).

| P-factor | Time | Carbohydrates | Acetic & formic acids | Lignin | Extractives | Others | Total |
|---|---|---|---|---|---|---|---|
| 200 | 1 h 41 min | 6.8 | 0.5 | 0.7 | 2.7 | 3.4 | 14.1 |
| 300 | 2 h 31 min | 7.8 | 0.7 | 0.8 | 2.7 | 2.6 | 14.6 |
| 400 | 3 h 21 min | 8.6 | 0.7 | 0.8 | 2.7 | 5.6 | 18.4 |
| 500 | 4 h 12 min | 9.5 | 0.7 | 0.8 | 2.7 | 5.7 | 19.4 |

In the cooking experiments, the most suitable P-factor was found to be 200, because higher P-factors resulted in lignin condensation reactions. This was verified by an increase in the kappa number (at constant conditions in cooking) with P-factors above 200.

The cooking and oxygen delignification experiments were carried out at Helsinki University of Technology (currently Aalto University). The experiments were first carried out with different P-factors in the water prehydrolysis stage. As indicated above, P-factor 200 was identified to be the most suitable one, and further experiments were carried out by using this P-factor. The conditions in the experiments were the following. The prehydrolysis and cooking were carried out in a 2 L digester using screened (7 – 13 mm) pine wood chips. The prehydrolyzate was discarded from the reactor after prehydrolysis by pressure relief, and no intermediate washing between water prehydrolysis and cooking was carried out. The temperature in the extraction was maximum 160 °C. The liquor-to-wood ratio was 5 in both prehydrolysis and cooking. In cooking, the effective alkali charge was 18.8 % on wood to cooking, the maximum temperature was 160 °C, and the H-factor (cooking time) was varied between 850 and 1450. A reference kraft cooking (with no water prehydrolysis) was run at the H-factor 1450, while keeping all the other process parameters constant. The conditions in oxygen delignification were constant for all pulp samples: an alkali charge of 0.075 times the kappa number, reaction time 60 min, temperature 95 °C, and $O_2$ pressure 6 bar. With varying H-factors, the cooking of prehydrolyzed chips resulted in varying kappa numbers and yields after cooking and oxygen delignification. The cooking experiment at H-factor 1000 was chosen as the data point adopted in the simulation model. Table 10 below presents the yields and kappa numbers of this and the reference cookings.

Table 10: Cooking and oxygen delignification of prehydrolyzed and reference chips (based on Kautto et al. 2010a).

| | Reference | Prehydrolyzed at P-factor 200 |
|---|---|---|
| **Cooking** | | |
| H-factor | 1450 | 1000 |
| Yield on wood | 46.2 % | 40 % |
| Kappa | 33 | 36 |
| **$O_2$ delignification** | | |
| Yield on wood | 44.7 % | 38.5 % |
| Kappa | 19 | 15 |

The abovementioned H-factor for the prehydrolyzed chips was chosen because the kappa number after oxygen delignification was in a suitable range of 15 – 20. Also cooking at H-factor 850 could have been selected. The kappa number after oxygen delignification was 19, and the yield on wood approximately 40 %. Choosing this data point for the simulation would have resulted in slightly more promising results: a somewhat lower increase in wood consumption and a smaller amount of organics in the chemical recovery.

In the simulation model, the mass balance over water prehydrolysis and cooking was compiled based on the abovementioned water prehydrolysis (Table 9, P-factor 200) and cooking experiments (Table 10). The liquor-to-wood ratio in the simulation model (4) was assumed to be lower than in the experiments (5). With an LTW of 4, 60 % of the generated prehydrolyzate was estimated to be recovered. The estimation was done based on the void volume of the wood material. For the calculation of energy balances, the heating values of black liquors from the cooking of unhyhdrolyzed and prehydrolyzed chips were measured. The measurements were made from the black liquors generated in the cooking trials at Helsinki University of Technology. In addition to black liquor, also all the residues generated in the processing of the prehydrolyzate were assumed to be combusted in the recovery boiler.

To evaluate the effects of water prehydrolysis and ethanol production on the operation of a kraft pulp mill, two simulation models were created: a reference kraft pulp mill with no prehydrolysis, and a kraft pulp and ethanol co-producing biorefinery. Both mills were assumed to be Nordic softwood pulp mills with a pulp output of 1000 Adt/d. Both literature and industry data were used to develop the simulation model of the reference mill. In addition to the experimental data, mainly literature data was used to simulate the new process steps of the biorefinery: prehydrolyzate processing, ethanol fermentation and recovery. The simulation models were developed by using WinGEMS 5.3 simulation software.

**Publication II**

In Publication II, the effect of water prehydrolysis on cooking, oxygen delignification, bleaching and beating, as well as the papermaking properties of the produced pulp were studied. The cooking experiments were carried out at Aalto University (former Helsinki University of Technology), while the pulp beating, bleaching and paper handsheet property tests were done at NabLabs Oy, Rauma.

Industrial pulp wood chips, mainly pine, but possibly containing also some amount of spruce, were used as the raw material. The chips were screened (7 – 13 mm) before the cooking trials. Water prehydrolysis was carried out in a 20 L digester with the liquor-to-wood ratio of 4.6 L/kg. The water in the digester was heated at a rate of 2 °C/min to reach the temperature of 150 °C. The temperature was then kept at 150 °C for 1 h 33 min, which corresponded to a P-factor of 200. After the set time, the prehydrolyzate was drained from the digester. No intermittent washing was carried out between prehydrolysis and cooking.

Cooking was carried out for three sets of chips. The unhydrolyzed reference chips were termed **Pulp 1**. These were pulped at the sulfidity level of 40 %. The prehydrolyzed chips were cooked at the sulfidity levels of 40 % (**Pulp 2**) and 20 % (**Pulp 3**). The cooking was carried out in the same 20 L digester as the water prehydrolysis. In all cookings, the liquor-to-wood ratio was 4.6 L/kg, the effective alkali level 20 % (as NaOH based on oven dry wood), and the maximum cooking temperature 160 °C (first heating from 80 °C to 160 °C at a rate of 1.5 °C/min, then maintaining the temperature at 160 °C). The cooking time (and the H-factor) was varied between between the sets of chips. The cooking of Pulp 1 was stopped at H-factor 1600 (cooking time of 3 h 51 min). Based on earlier experiments (presented in Publication I), it was assumed that the prehydrolyzed chips would require lower H-factors and respond better to oxygen delignification. The cooking times of the prehydrolyzed chips were therefore shorter, and they had a higher target kappa number after cooking. Pulp 2 had H-factor 1000 (2 h 22 min) and Pulp 3 1300 (3h 6 min). After cooking, the produced pulps were removed from the digester, centrifuged, homogenized and weighed (the dry solids content measured according to SCAN-C 3:78). The metal content of the pulps was also measured (by using inductively coupled plasma atomic emission spectroscopy).

The pulps were then screened (TAP031 screener with a slot size of 0.25 mm). The dry solids content of the accept and reject fractions were analyzed (SCAN-C 3:78). The pulps were then oxygen-delignified and bleached. Oxygen delignification was carried out in a 16 L reactor with 600 grams of pulp. The conditions in this stage were constant for all pulp samples. The target kappa number after the stage was 15. Unpressurized laboratory bleaching was carried out with 300 gram pulp batches that were put in plastic bags. The bags were then placed in a hot water bath. The bleaching sequence was DED (chlorine dioxide - alkaline extraction - chlorine dioxide). The pulps were washed after oxygen delignification and all bleaching stages. Chemical charges in the $D_0$ and E stages were calculated based on the kappa number after oxygen delignification, while the dosage in the $D_1$ stage was the same for all pulps. The target ISO brightness in bleaching was 74 %. Table 11 below presents the conditions in oxygen delignification and bleaching.

Table 11: Conditions and chemical charges in oxygen delignification and bleaching (based on Kautto et al. 2010b)

| Sequence | O | $D_0$ | E | $D_1$ |
|---|---|---|---|---|
| Pulp consistency, % | 10 | 10 | 10 | 10 |
| Active chlorine charge, % | | 0.2 x incoming kappa | | 1 |
| NaOH charge, % | 2 | | 0.6 x $D_0$ charge | |
| Temperature, °C | 90 | 60 | 60 | 70 |
| Time, min | 30 | 45 | 75 | 180 |
| Pressure, bar | 5 | | | |
| Target end pH | | ~2 | ~12 | ~3.6 |

The viscosity of the pulp samples was measured after the oxygen delignification and bleaching stages E and $D_1$ according to ISO 5351-1:1981. The ISO brightness (ISO 2470:1999) was measured after oxygen delignification and the E and $D_1$ stages, and the kappa numbers (ISO 302:2004) before and after oxygen delignification.

The mechanical properties of the bleached pulps were evaluated in handsheet testing (ISO 5270:1998). Pulp refining was carried out in a PFI mill (ISO 5264-2:2002). Hand sheets with different degrees of beating were prepared (ISO 5269-1:1998), and the freeness (CSF) was measured (ISO 5267-2:2001).

### 4.5.2 Organosolv pulping (Publications III and IV)

The organosolv pulping process was evaluated based on a simulation model which was done by using Aspen PLUS$^{TM}$ (V7.1) simulation software. Both the conceptual process design and the simulation model were developed on the basis of literature data. The simulation model was used to evaluate the overall mass and energy balances. The balances were then used as input in an economic analysis of the process concept. The economic analysis was carried out by using the minimum ethanol selling price (MESP, see subchapter 2.1.4). This enabled comparing the organosolv process to a dilute acid pretreatment -based ethanol production process. The development of the conceptual process design and economic analysis are described in more detail below.

**Publication III**

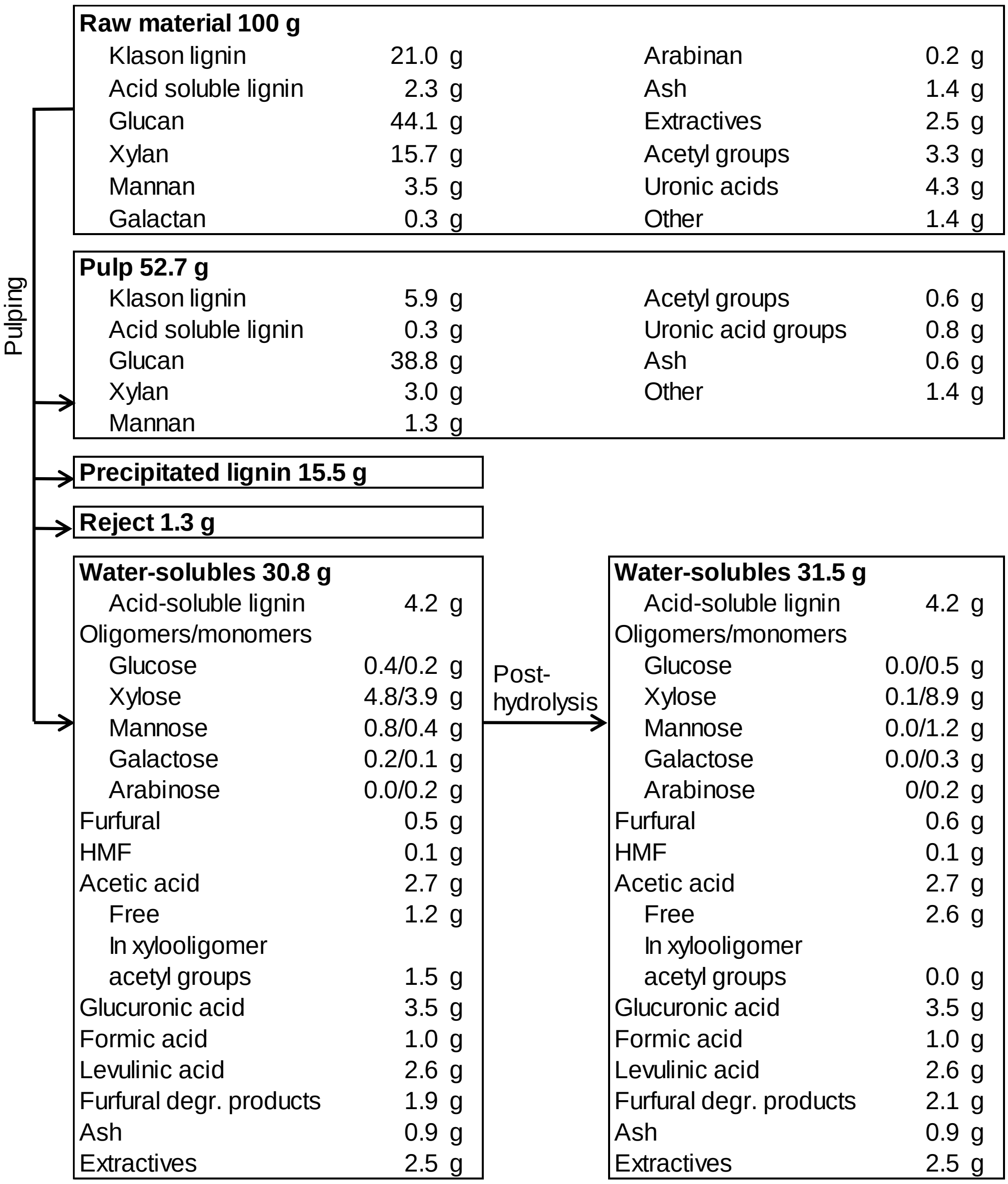
The conceptual process design and the simulation model of the organosolv cooking -based biorefinery were developed in Publication III. The process design and simulation model were compiled by using literature sources and Aspen PLUS 7.1$^{TM}$ simulation software. The key literature sources and assumptions concerning the development of the model are reviewed below.

The conceptual process design over the pulping section of the process was developed by following partially the process schemes outlined in the works of Agar et al. (1998) and Pan et al. (2005). The process steps downstream of the organosolv cooking were in turn developed by following the NREL dilute acid bioethanol production process (Humbird et al. 2011) as closely as possible. Also the raw material intake (as dry, debarked raw material) was assumed to be the same as in the NREL study (2000 t/day).

The mass balance over organosolv cooking was calculated based on the laboratory work carried out by Pan et al. (2006). They cooked hybrid poplar chips (fraction passing a 6.35 mm round screen) in 2 L reactors in a mixture of ethanol and water, using sulfuric acid as a catalyst. The cooking temperature and time, as well as the ethanol concentration and catalyst dosage were varied in the trials. So-called center point conditions (leading to higher or comparable yield of total and cellulose and xylose recoveries than other conditions) of the study (cooking temperature 180 °C, time 60 min, 1.25 % $H_2SO_4$ on dry wood, 50 vol-% ethanol concentration) were followed in the development of the simulation model. The mass balance closure at the center point conditions of the study was approximately 90 %. Certain adjustments were therefore carried out to close the mass balance over cooking (for details, see Publication III). While the liquor-to-wood ratio in the experiments of Pan et al. (2006) was 7, it was assumed to be 5 in the simulation model.

Since the carbohydrates present in the spent cooking liquor after cooking were to a considerable degree present in an oligomeric form, a post-hydrolysis step was carried out after flashing of the cooking liquor to convert the oligomers to monomeric sugars. A kinetic model presented by Garrote et al. (2001) was used to model the reactions taking place in the step. At a temperature of 135 °C and sulphuric acid concentration of 0.3 wt-%, a reaction time of 1 hour was found, based on the kinetic model, to be suitable to convert a majority of the oligomers to monomers and to avoid excessive sugar degradation.

After post-hydrolysis, the spent cooking liquor was further flashed in two stages to recover heat and part of the ethanol solvent, followed by dilution of the cooking liquor with water to an ethanol concentration of 15 vol-% to precipitate lignin from the pulping liquor (based on Agar et al. 1998). The amount of lignin precipitated in these conditions was evaluated based on the study of Pan et al. (2006). Instead of diluting with water, another alternative to precipitate the lignin would have been to decrease the ethanol concentration in the spent cooking liquor by evaporation or stripping. This would have reduced the amount of water circulating in the system and thereby decreased the energy consumption. Dilution with water was, however, chosen as the precipitation method used in the process design of Publication III for two reasons. Firstly, it has been described to be the precipitation method utilized in the Lignol organosolv process (see e.g. Agar et al. 1998; Hallberg et al. 2008; Pye and Rushton 2013). Secondly, precipitation of lignin by stripping has been described to result in fouling problems in the stripper and a lignin product that is difficult to handle and convert into a powder (Agar et al. 1998). It was therefore assumed in the development of the process design that dilution with water would be the most suitable precipitation method for the production of a higher-valued lignin product. The precipitated lignin solids were separated with a filter and dried in spray driers using natural gas as the fuel. Figure 8 below presents a schematic mass balance over organosolv cooking, post-hydrolysis and lignin separation.



**Raw material 100 g**

| | | | |
|---|---|---|---|
| Klason lignin | 21.0 g | Arabinan | 0.2 g |
| Acid soluble lignin | 2.3 g | Ash | 1.4 g |
| Glucan | 44.1 g | Extractives | 2.5 g |
| Xylan | 15.7 g | Acetyl groups | 3.3 g |
| Mannan | 3.5 g | Uronic acids | 4.3 g |
| Galactan | 0.3 g | Other | 1.4 g |

**Pulp 52.7 g**

| | | | |
|---|---|---|---|
| Klason lignin | 5.9 g | Acetyl groups | 0.6 g |
| Acid soluble lignin | 0.3 g | Uronic acid groups | 0.8 g |
| Glucan | 38.8 g | Ash | 0.6 g |
| Xylan | 3.0 g | Other | 1.4 g |
| Mannan | 1.3 g | | |

**Precipitated lignin 15.5 g**

**Reject 1.3 g**

| Water-solubles 30.8 g | | Water-solubles 31.5 g | |
|---|---|---|---|
| Acid-soluble lignin | 4.2 g | Acid-soluble lignin | 4.2 g |
| Oligomers/monomers | | Oligomers/monomers | |
| Glucose | 0.4/0.2 g | Glucose | 0.0/0.5 g |
| Xylose | 4.8/3.9 g | Xylose | 0.1/8.9 g |
| Mannose | 0.8/0.4 g | Mannose | 0.0/1.2 g |
| Galactose | 0.2/0.1 g | Galactose | 0.0/0.3 g |
| Arabinose | 0.0/0.2 g | Arabinose | 0/0.2 g |
| Furfural | 0.5 g | Furfural | 0.6 g |
| HMF | 0.1 g | HMF | 0.1 g |
| Acetic acid | 2.7 g | Acetic acid | 2.7 g |
| Free | 1.2 g | Free | 2.6 g |
| In xylooligomer acetyl groups | 1.5 g | In xylooligomer acetyl groups | 0.0 g |
| Glucuronic acid | 3.5 g | Glucuronic acid | 3.5 g |
| Formic acid | 1.0 g | Formic acid | 1.0 g |
| Levulinic acid | 2.6 g | Levulinic acid | 2.6 g |
| Furfural degr. products | 1.9 g | Furfural degr. products | 2.1 g |
| Ash | 0.9 g | Ash | 0.9 g |
| Extractives | 2.5 g | Extractives | 2.5 g |

Figure 8: Schematic dry solids mass balance over organosolv cooking, post-hydrolysis and lignin separation assumed in the model (from Kautto et al. (2013), figure layout partially adopted from Pan et al. (2006), and balances based on Pan et al. (2006), Sannigrahi et al. (2009) and Garrote et al. (2001)), (Biomass Conversion and Biorefinery, Design and simulation of an organosolv process for bioethanol production, 3(3), 2013, pp. 199-212, Kautto et al.,"With permission of Springer").

After lignin separation, the spent cooking liquor was split and fed to two heat-integrated distillation columns for ethanol recovery. The pressures of the two columns were set so that the heat from the condenser of the higher-pressure column was utilized in the reboiler of the lower-pressure column. The design of the distillation columns was done with the Aspen simulation software. The minimum number of equilibrium stages and the minimum reflux ratio to obtain a certain ethanol recovery and ethanol concentration in the distillate were evaluated first. The actual number of stages and reflux ratio were then selected by using certain heuristic rules (see e.g. Luyben 2006 for an overview on distillation design using Aspen simulation software). A similar method was used in designing other distillation columns in the model. Furfural, creating a minimum-boiling heterogeneous azeotrope with water, was recovered in the simulation model as a side-draw from the ethanol recovery distillation columns. The furfural-rich side-draw was further purified by decantation and distillation.

The bottoms stream from the recovery columns, containing hemicellulosic sugars, was evaporated and conditioned before fermentation. The evaporation was assumed to be carried out in a four-effect evaporation train to achieve a dry solids content which would not result in an ethanol concentration higher than the reported ethanol tolerance limit of the fermenting microorganism (60 g/L, see Humbird et al. (2011)). As indicated by Agar et al. (1998), lower molecular weight lignin was assumed to form a tarry organic phase at a dry solids content of approximately 15 wt-% (between evaporation effects 2 and 3) that could be separated by decantation. After evaporation, the residual lignin was assumed to be removed by extraction with furfural, as outlined in the work of Agar et al. (1998). As discussed in Publication III, this step could have been potentially omitted, particularly since this lignin fraction was not assumed to be utilized. After extraction, the hemicellulosic sugar stream was assumed to be conditioned with ammonia to a pH of approximately 5, as outlined in the NREL study (Humbird et al. 2011), followed by feeding the stream to fermentation.

Acetic and formic acids accumulated partially in the vapor condensates of the evaporation train. Acetic acid was assumed to be recovered from the condensates by extraction and distillation, as outlined in the patent of Kanzler and Schedler (1983). The extraction step was carried out with trioctyl phosphine oxide (TOPO) in an undecane diluent. The step was modelled based on distribution coefficients published in the literature. The purification of the extracted acetic acid took place in three distillation columns.

The pulp from organosolv cooking was washed first with an ethanol mixture to avoid lignin precipitation and then with water to recover ethanol. The washing stages were modelled assuming a pressure diffuser for the first and medium consistency drum displacer (DD) washer for the second washing stage. The pressure diffuser had inlet and outlet consistencies of 10 % and a dilution factor (difference of wash liquor flow and liquor flow contained in the washed pulp per dry mass flow of pulp) of 1.7, while the DD washer had inlet and outlet consistencies of 10 % and 16 %, respectively, and a dilution factor of 10. The wash filtrates from the DD washer were fed countercurrently to the pressure diffuser. Instead of assuming a pressure diffuser and a DD washer in the design, also other configurations could certainly have been assumed. One typical approach would have been to assume either a pressure diffuser or a DD washer for the first stage and washing press for the second stage. After washing, the pulp was first screened and then fed to enzymatic hydrolysis.

Although the pretreatment and raw materials differed between the studied organosolv process concept and the NREL study (Humbird et al. 2011), the enzymatic hydrolysis of the pulp produced in organosolv pulping, as well as the fermentation were designed based on the NREL study. In the enzymatic hydrolysis step, 90 % of cellulose and 82 % of xylan and other hemicelluloses were assumed to be converted to monomeric sugars. In the study of Pan et al. (2006), organosolv pulp was found to have a better response to enzymatic hydrolysis than steam explosion -pretreated wood. Since Publication III aimed at comparing the two pretreatment steps, also a higher conversion rate for the organosolv pulp could therefore have been adopted. It should, however, be kept in mind that enzymatic hydrolysis is always a trade-off between enzyme dosage and enzymatic conversion, and the optimal types of enzymes and enzyme dosage may vary between pretreatments. As discussed in Publication IV, the conversion rates in industrial-scale enzymatic hydrolysis could furthermore be lower than those obtained in smaller-scale experiments. Assuming the conversion rate as the one in the NREL study (Humbird et al. 2011) was therefore considered justifiable.

In the fermentation stage, 95 % of glucose and 85 % of xylose and arabinose were assumed to be fermented to ethanol, based on the NREL study (Humbird et al. 2011). The conceptual process design included also a five-stage seed train for the production of the fermenting microorganism. The seed train was modeled based on the NREL study. In total 10 % of the sugars fed to the fermentation stage were directed to the seed train.

Ethanol recovery after fermentation was modelled based on the NREL study (Humbird et al. 2011). The fermentation broth was first fed to a beer column where $CO_2$ was separated as a distillate, most organics and water as a bottoms stream and most ethanol as a vapor side draw. The side draw was then fed to a rectification column to concentrate the ethanol to a concentration of 92.5 %, followed by final purification with molecular sieves. The bottoms stream from the first column was fed to a pressure filter to separate insoluble solids, followed by the combustion of the filter cake and feeding of the filtrate to waste water treatment. The waste water treatment plant was not specifically modelled in the simulation model, but the amount of biogas and sludge generated in the plant were estimated based on the NREL study (Humbird et al. 2011).

The bark, biogas and sludge from the waste water treatment plant and all organic residues from the process were combusted to produce steam and electricity. Natural gas was assumed to be used as an external energy source to cover the steam demand. The boiler and turbine were modelled based on the NREL study (Humbird et al. 2011). The electricity consumption of the process concept was estimated based on the NREL study and the report of Fogelholm and Suutela (1999).

In addition to the technical evaluation of the organosolv process concept, also approximate $CO_2$ emissions of the process concept were calculated. The calculation took account of only the natural gas consumption of the process.

**Publication IV**

An economic analysis of the organosolv process was done in Publication IV. The analysis was based on the conceptual process design and simulation model developed in Publication III. In the economic analysis, the investment and operating costs, as well as co-product revenues were estimated first. These were then used to calculate the so-called Minimum Ethanol Selling Price (MESP), which is the minimum price of ethanol required to cover the costs of the operation and make a certain return on the invested capital. The lower the MESP, the more cost competitive the ethanol producing process. The MESP of the organsolv process was then compared to that of the dilute acid pretreatment -based process presented in the NREL study (Humbird et al. 2011). The study was carried out in the 2013 value of the US dollar. All prices and costs that were from earlier years were indexed to 2013.

The investment cost of the organosolv process was evaluated based particularly on the developed conceptual process design and simulation model, the NREL study (Humbird et al. 2011), the Aspen Process Economic Analyzer 7.1 and industry estimates. For the investment cost analysis, the organosolv process was divided into process areas. Process areas that were considered similar to those in the dilute acid process were estimated based on the NREL study (Humbird et al. 2011). Process areas specific to organosolv cooking, as well as solvent and co-product recovery were in turn estimated primarily by using the Aspen Process Economic Analyzer and industry estimates. Table 12 lists the process areas and their costing bases.

Table 12: Process areas and bases of costing (based on Kautto et al. 2014).

| Process area | Description | Basis of costing | Source and scaling basis |
|---|---|---|---|
| Feed handling | Wood yard (receiving, debarking, and chipping of wood) | Process area | Industry estimate |
| Pretreatment and lignin recovery | Cooking, pulp washing, post hydrolysis, precipitation, and drying of lignin | Individual equipment | Industry estimate,<br>Aspen Process Economic Analyzer 7.1, Humbird et al. (2011) |
| Solvent and furfural recovery | Solvent and furfural recovery columns | Individual equipment | Aspen Process Economic Analyzer 7.1, Humbird et al. (2011) |
| Conditioning of the hemicellulosic sugar stream | Evaporation, separation of low molecular weight lignin, ammonia treatment | Individual equipment | Aden et al. (2002), Aspen Process Economic Analyzer 7.1, Humbird et al. (2011) |
| Acetic acid recovery | Extraction of acetic acid from evaporator condensates, distillation to a pure acetic acid product | Individual equipment | Aspen Process Economic Analyzer 7.1 |
| Hydrolysis and fermentation | Enzymatic hydrolysis and fermentation to ethanol | Individual equipment | Humbird et al. (2011) |
| Ethanol product and solids recovery | Distillation of the pure ethanol product, filtration of distillation bottoms solids | Individual equipment | Humbird et al. (2011) |
| Wastewater treatment | Anaerobic and aerobic treatment systems | Process area | Humbird et al. (2011), assumed to be similarly sized |
| Storages | End-product and raw material storages | Process area | Humbird et al. (2011), assumed to be similarly sized |
| Boiler and turbine | Combustion of organic residues and purchased natural gas and generation of steam and electricity | Process area | Humbird et al. (2011), scaled on the amount of combustion heat |
| Utilities | Cooling and chilled water, plant/instrument air, and process water systems | Process area | Humbird et al. (2011), cooling and chilled water systems scaled on cooling duty, everything else assumed to be similar |

Based on the cost of installed equipment, the total capital investment, including other direct and indirect costs and working capital, was calculated based on the factors presented in the NREL study (Humbird et al. 2011). The factors are presented in Table 16 in subsection 5.4. The investment costs were varied by 30 % in the sensitivity analyses.

Concerning the operating costs, the feedstock (hybrid poplar) price was estimated based on a literature review to be 85 USD/dry t as delivered to the plant gate. In sensitivity analyses the price was varied in the range of 70 to 100 USD/dry t. The base case enzyme cost (as indexed to 2013 dollars) and dosage were based on the NREL study (Humbird et al. (2011), 5270 USD/t and 0.02 g enzyme/g cellulose). A more conservative enzyme cost (price 3700 USD/t, dosage 0.06 g enzyme/g cellulose, based on Novozymes (2011)), was used in the sensitivity analyses. The NREL study (Humbird et al. 2011) and various other sources were used to estimate the prices and costs related to other variable and fixed costs, such as chemicals, energy and personnel. The base case sales price of lignin was set at 450 USD/t. Also the lignin price was varied in the sensitivity analyses.

Annual cash flows and MESP were calculated by following the NREL study (Humbird et al. 2011). The plant was assumed to be constructed in three years and be operational for 30 years after the construction. The plant was assumed to be on-line approximately 350 days per year. Table 13 presents the assumed schedule and cash flow in planning and engineering, construction and start-up and in detail.

Table 13: Schedule and cash flow in plant planning and engineering, construction and start-up (based on Kautto et al. 2014).

| Phase | Time, months | Cash flow |
|---|---|---|
| Planning and engineering | 0 – 12 | 8 % of project investment |
| Construction | 12 – 24<br>24 – 36 | 60 % of project investment<br>32 % of project investment +working capital |
| Start-up | 36 – 39 | 50 % of production<br>75 % of variable costs<br>100 % of fixed costs |
| Full production | 39 → | |

The discount rate used in the MESP calculation was 10 %. The capital investment was financed with 40 % equity and 60 % loan. The interest on the loan was 8 % and it was paid back in 10 years. The corporate tax rate was 35 %. The steam and power production plant was depreciated in 20 years, and the rest of the equipment in 7 years. In the sensitivity analyses, the discount rate was increased from 10 % to 20 %.

In addition to the base case MESP calculation, sensitivity analyses were carried out in Publication IV. Both technical (internal) and exogenous (external, market-related) parameters were analyzed. The lignin sales price, as well as feedstock, enzyme and investment costs and the discount rate were included as exogenous parameters. The technical parameters and their variation are described briefly below.

The hybrid poplar pulp produced through ethanol organosolv cooking was in this study assumed to have the same enzymatic conversion as the dilute acid -pretreated corn stover in the NREL study (Humbird et al. 2011) (cellulose to glucose conversion of 90 %). Organosolv pulps have, however, been found to have a good response to enzymatic hydrolysis, with Pan et al. (2006) reporting cellulose to glucose conversion of 96 % at approximately the same enzyme loading as in the NREL study. The effect of the potentially improved enzymatic conversion of organosolv pulp was studied by setting the conversion 6 percentage points higher for all carbohydrates (both for cellulose and hemicelluloses). Since the conversion rates in industrial-scale enzymatic hydrolysis could be significantly lower, a conversion rate of 80 % for all carbohydrates was studied as a more conservative scenario.

In the base case scenario, 85 % of hemicellulosic C5 sugars (particularly xylose) were assumed to be fermented to ethanol, while mannose and galactose (hemicellulosic C6 sugars) were not assumed to be fermented, as outlined in the NREL study (Humbird et al. 2011). Since several other studies (see e.g. Aden et al. 2002) have assumed the fermentation of mannose and galactose, a more optimistic scenario assumed the fermentation of these sugars (85 % conversion). The conversion of hemicellulosic sugars in the fermentation could, however, well be lower than assumed in the base case scenario. The fermentation of xylose and other hemicellulosic sugars has generally proven challenging (see e.g. Aden et al. 2002). In addition, the aqueous stream from organosolv cooking could initially contain relatively high amounts of sugar degradation products and other inhibitory compounds. Although the conditioning procedure was assumed to decrease the amount of these compounds to a level low enough for fermentation, the residual inhibitory compounds could affect the fermentation. No data was available on the fermentability of the aqueous stream after conditioning. The processing of the aqueous stream could furthermore result in greater sugar losses than assumed. A lower conversion rate, with 50 % conversion for hemicellulosic C5 sugars and 0 % for C6 sugars, was therefore assumed as the more pessimistic scenario.

Various assumptions related to the conceptual process design would have an effect on the energy consumption. The steam and electricity consumption was varied by 30 % to capture the effect of this inherent uncertainty.

### 4.5.3 Summary and critical review of the methods utilized in Publications I – IV

Figure 9 below summarizes the methods utilized in evaluating the two process concepts. The figure also lists the main outcomes of the evaluations, which are described in closer detail in Chapter 5.

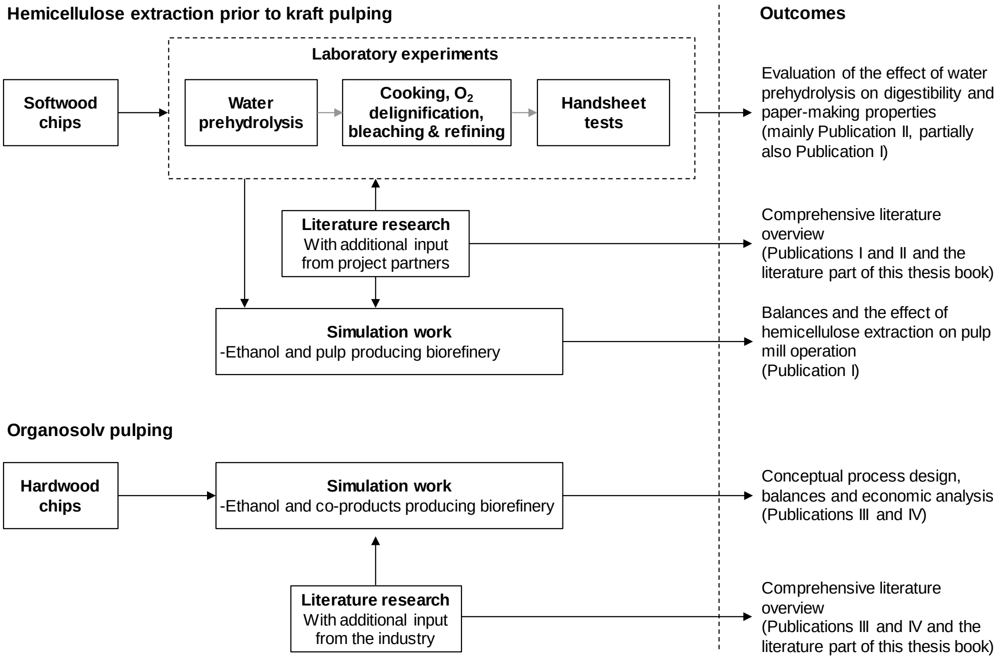


Figure 9: The main working methods applied in the thesis.

## Critical review of the applied methods

As described in subchapters 4.5.1 and 4.5.2 and summarized in the figure above, literature research and simulation work were carried out in evaluating the studied process concepts. Laboratory experiments were furthermore carried out related to the hemicellulose extraction concept. In this subsection, the applied methodology is evaluated critically. Are the applied methods relevant and necessary from the perspective of the main research question of the thesis of whether the two studied processes (pre-extraction of hemicelluloses prior to kraft pulping and organosolv pulping) are feasible biomass fractionation and biorefinery concepts?

A simulation model of an ethanol and pulp -producing biorefinery was developed on the basis of laboratory experiments in Publication I. More detailed laborotary experiments on water prehydrolysis, cooking, $O_2$ delignification, bleaching, refining and handsheet properties were carried out in Publication II. As described below in Chapter 6, the key drawbacks of the hemicellulose extraction concept were a decreased yield on wood, an increased load on evaporation and the recovery boiler, low concentration and difficult processability of the produced prehydrolyzate, and a small ethanol output. The effects on the quality of pulp were furthermore found to be inconclusive at best. For these reasons, the concept could not be considered attractive for the production of bulk-type paper-grade pulp and ethanol. In retrospect, most of these effects could have been identified in the the laboratory experiments carried out in Publications I and II and in mass and energy balances calculated around the extraction and cooking stages. As also the reviewed literature supported and complemented these findings, the key question is whether it was necessary to develop a simulation model of an ethanol and pulp -producing biorefinery? Would the laboratory experiments, literature review and mass and energy balance calculations been sufficient to arrive at an answer to the main research question? The key benefit of the developed simulation model was the possibility to study the technical aspects of integrating the hemicellulose extraction and bioethanol production processes to a pulp mill. As the key drawbacks of the concept could, however, have been identified without a sophisticated simulation model, it can in retrospect be stated that the development of the simulation model did not provide major insights into the evaluation of the attractiveness of the concept.

In the evaluation of the organosolv pulping concept, the situation was entirely different. While numerous laboratory experiments on organosolv pulping had been published, the key aspect in the evaluation of the organosolv process was to study the whole process concept from pulping to ethanol production and solvent and co-product recovery. The evaluation required the development of a comprehensive conceptual process design, calculation of mass and energy balances, and estimation of operating and capital costs. With for example several distillation columns, this would have been difficult without a proper simulation model. The model was therefore an essential part of the comprehensive and systematic evaluation of the process concept.

# 5 Review of the publications and research findings

The objectives, results and main contribution of the four research publications constituting the second part of this thesis are summarized in this chapter. After reviewing the publications separately, the publications are first summarized in subchapter 5.5. The linkages of the publications to the research questions (laid out in subchapter 1.3) are then discussed in subchapter 5.6.

## 5.1 Publication I: Effects of integrating a bioethanol production process to a kraft pulp mill

*Objective*

The objective of the first publication was to develop a simulation model for a pulp and ethanol producing pulp mill biorefinery based on hemicellulose extraction technology. The development of the simulation model was based on experimental data on the extraction, cooking and oxygen delignification stages. The simulation model was used to establish mass and energy balances over the studied stages as well as to evaluate the effects of the extraction stage on the overall operation of the pulp mill. WinGEMS (version 5.3) was used to develop the simulation model. The publication provided input to the research questions *Q1* and *Q2*.

*Results and main contribution*

With the establishment of the mass balance over hemicellulose extraction, cooking and oxygen delignification as well as ethanol production, hemicellulose extraction through a water prehydrolysis process was found to decrease the yield on wood after cooking and oxygen delignification and result in a relatively small ethanol output. Compared to a reference case with no extraction, the decreased yield on wood results in either decreased pulp production if the wood consumption is kept constant or increased wood consumption if the pulp production is kept constant. In the publication, pulp production was assumed to be kept constant. At a pulp production of 1000 air dry tons (Adt) per day (d), extraction of 14.1 % of wood material prior to cooking increased the wood consumption by 16 %, from 2327 to 2703 oven dry tons (Odt)/d of undebarked wood. The hemicellulose extraction enabled the production of 40 t/d of ethanol.

The increased wood consumption resulted in an increased load on the debarking and chipping equipment and the bark boiler. The yields on wood corresponding to the 16 % wood consumption increase after cooking and oxygen delignification were 40 % and 38.5 % in the hemicellulose extraction case and 46.2 % and 44.7 % in the reference case, respectively. The digester yield, defined as the yield in cooking on extracted chips, was calculated to be 46.6 % with hemicellulose extraction. The similar digester yields (46.6 % and 46.2 %) indicated that both the amount of chips fed to the digester and the wood material dissolved in cooking would be similar. The amount of cooking chemicals was also expected to be similar. A lower H-factor was, however, required for the pre-extracted chips, indicating that either a shorter cooking time or lower temperature could be applied for the pre-extracted chips. The effects of hemicellulose extraction on the fiberline of the pulp mill were evaluated in closer detail in Publication II.

In the chemical recovery system of the pulp mill, the key effects of hemicellulose extraction were seen in the evaporation plant and the recovery boiler. The heat load to the recovery boiler was found to be increased for three reasons. Part of the prehydrolyzate (hemicellulose-containing liquid phase produced in water prehydrolysis) could be separated in the extraction and utilized in the production of bioethanol, while part was retained in the pores of the wood chips and carried over to cooking. This increased the amount of organics in the black liquor, increasing the heat load to the recovery boiler of the pulp mill. Additionally, various residues from the processing of the prehydrolyzate to ethanol were assumed to be evaporated in the evaporation plant and combusted in the recovery boiler, increasing the organics content in the black liquor. With part of the carbohydrates separated in the prehydrolysis step prior to cooking, relatively more lignin than carbohydrates were dissolved in cooking. As lignin has a higher heating value than carbohydrates, this increased the heat load to the recovery boiler further. The overall effect on the recovery boiler was found to be considerable, with the heat load increased by 31 %.

With the prehydrolyzate carried over to cooking in wood chip pores, the water content of the weak black liquor was found to be increased, increasing the load on the evaporation plant. Feeding the prehydrolyzate residues to the evaporation train increased the load further. After mild acid hydrolysis and liming the prehydrolyzate had a low solids content of 2.5 %. It was assumed to be evaporated prior to fermentation to increase its solids content. The evaporation was assumed in the simulation model to be coupled with the black liquor evaporation plant, with secondary steam from the last effect of the evaporation train used in the evaporation of the prehydrolyzate. With the increased amount of water fed to the evaporation plant and its coupling with the evaporation of the prehydrolyzate, the steam demand (27 %) and required heat transfer area (65 %), were increased, and in addition two effects were required for the evaporation of the prehydrolyzate. In addition to the increased steam demand in the evaporation, especially the prehydrolysis and distillation of the ethanol stream increased also the steam demand of the mill. With the increased heat load on the bark and recovery boilers, the electricity generation was, however, found to be increased.

The main contribution of the first publication can be considered to be the establishment of the mass and energy balances over a pulp and ethanol -producing biorefinery, and demonstration of the effect of hemicellulose extraction and ethanol production on the overall operation of a pulp mill.

## 5.2 Publication II: Digestibility and paper-making properties of prehydrolyzed softwood chips

*Objective*

The objective of the second publication was to evaluate the effect of hemicellulose extraction on pulping and papermaking properties through laboratory experiments. The evaluation was carried out in a comprehensive manner, covering the whole fiber line from the cooking of extracted chips to oxygen delignification, bleaching and testing of bleached pulps. The publication provided input to research question *Q2*.

*Results and main contribution*

Hemicelluloses were extracted in a water prehydrolysis step at conditions relatively similar to those in Publication I. Prehydrolyzed and reference chips were then cooked at different sulfidity levels, followed by oxygen delignification. Altogether three different pulps were studied. The reference pulp, which was not prehydrolyzed before cooking, was cooked at a sulfidity level of 40 % and was termed **Pulp 1**. The prehydrolyzed chips were cooked at sulfidity levels of 40 % (**Pulp 2**) and 20 % (**Pulp 3**). The target kappa number (the factor describing the amount of residual lignin in pulp) after oxygen delignification was 15 for all pulps. Based on laboratory experiments published in Publication I, it was known that prehydrolyzed chips require milder conditions in cooking and respond better to oxygen delignification. The prehydrolyzed chips were therefore cooked at lower H-factors, with Pulp 2 cooked at H-1000 and Pulp 3 at H-1300, while the reference chips (Pulp 1) were cooked at H-1600. All pulps were then oxygen-delignified in constant conditions.

The results obtained in Publication II confirmed that lower H-factors could be used in the cooking of prehydrolyzed chips than with the reference chips. At similar sulfidity levels of 40 %, the reference chips (Pulp 1) cooked at H-factor 1600 and the prehydrolyzed chips (Pulp 2) cooked at H-factor 1000 resulted in similar kappa numbers of 25.4 and 24.4, respectively. The decrease in H-factor from 1600 to 1000, corresponding to a shortening of the cooking time by 39 %, indicated that the digestibility of the prehydrolyzed chips was higher. The wood consumption increase (at constant pulp production) resulting from a decrease in the yield on wood was found to be at a level similar to that presented in Publication I.

The constant conditions in oxygen delignification resulted in a considerably higher kappa reduction with the prehydrolyzed pulp than with the reference pulp. This improved response to $O_2$ delignification was attributed to decreased hemicellulose content, with the higher initial kappa number possibly also attributing to the improvement. In the bleaching trials, the prehydrolyzed pulp cooked at 40 % sulfidity (Pulp 2) was found to consume a lower amount of bleaching chemicals in a DED bleaching sequence compared to the reference pulp (Pulp 1, cooked at the same sulfidity) to obtain a target ISO brightness of approximately 74 %. In the beating of the pulps, a considerably higher number of revolutions in a PFI mill were required to obtain a given tensile index for the prehydrolyzed pulp than for the reference pulp. In the handsheet tests, the reduction in the hemicellulose content of the prehydrolyzed pulps was found to decrease the tensile index and increase the tear index. The changes in the handsheet properties resulting from the prehydrolysis step were generally attributed to decreased interfiber bonding. Table 14 below summarizes the main findings of Publication II.

Table 14: Summary of the main findings of Publication II (based on Kautto et al. 2010b).

| | Pulp 1 (reference pulp, sulfidity 40 %) | Pulp 2 (prehydrolyzed, sulfidity 40 %) | Pulp 3 (prehydrolyzed, sulfidity 20 %) |
|---|---|---|---|
| **Cooking** | | | |
| H-factor | 1600 | 1000 | 1300 |
| Yield on wood, % | 49.5 | 42.3 | 42.8 |
| Kappa | 25.4 | 24.4 | 33.1 |
| Residual alkali, g/L | 7.9 | 9.8 | 10.5 |
| Viscosity, ml/g | 1280 | 1320 | 1280 |
| **Oxygen delignification** | | | |
| Yield on wood, % | 48.5 | 41.5 | 41.6 |
| Kappa | 16.1 | 13.6 | 16.4 |
| ISO-brightness, % | 37.7 | 42.5 | 39.4 |
| Viscosity, ml/g | 1055 | 1070 | 1010 |
| **DED bleaching** | | | |
| $ClO_2$ consumption, as total active chlorine (kg Cl/t of pulp) | 42.2 | 37.2 | 42.8 |
| Viscosity, ml/g | 998 | 990 | 935 |
| ISO-brightness, % | 74.1 | 73.7 | 71.9 |
| **Refining and properties of refined pulp**[1] | | | |
| Cellulose/hemicellulose ratio | 4.9 | 10.6 | 10.1 |
| Beating revolutions in a PFI mill | 525 | 2395 | 1585 |
| Freeness (CSF), ml | 684 | 668 | 677 |
| Tensile index, Nm/g | 67.1 | 58.2 | 62.1 |
| Tear index, $Nm^2/kg$ | 16.2 | 22.6 | 23.9 |
| Tensile stiffness index, kNm/g | 6.87 | 6.17 | 6.60 |

[1] Values interpolated to a density of 700 $kg/m^3$

The main contribution of the second publication can be considered to be the systematic evaluation of the effects of hemicellulose extraction through water prehydrolysis on the pulp mill fiberline and the quality of the pulp. Together with Publication I, this enabled a comprehensive evaluation of water prehydrolysis-based hemicellulose extraction for the co-production of pulp and ethanol.

## 5.3 Publication III: Design and simulation of an organosolv process for bioethanol production

*Objective*

The objective of the third publication was to present a conceptual process design and simulation model of an organosolv pulping -based biorefinery producing ethanol, organosolv lignin, acetic acid, and furfural. Aspen PLUS$^{TM}$ (V7.1) was used to develop the simulation model. With the development of the simulation model, a further aim of the publication was to establish the mass and energy balances over the studied biorefinery concept and to compare the process to a more standard dilute acid pretreatment -based bioethanol production process described in the NREL technical report (Humbird et al. 2011). The publication provided input to the research questions *Q3* and *Q4*.

*Results and main contribution*

Based on the analysis of publicly available information, a conceptual process design and simulation model of an organosolv pulping -based biorefinery concept was developed and presented in the publication. The feedstock to the process was assumed to be hybrid poplar. The feedstock intake was 2350 Odt/d of undebarked wood, resulting in 2000 Odt/d of debarked chips fed to the organosolv process.

In the modeled process, the debarked hardwood chips were first delignified in organosolv cooking. In cooking, an ethanol-water mixture, with sulfuric acid as a catalyst, was used to dissolve the lignin and hydrolyze the hemicelluloses. The resulting pulp was first washed and then enzymatically hydrolyzed to sugars. The spent cooking liquor was first flashed and then sent to a post-hydrolysis step where the oligomers present in the liquor were converted to monomeric sugars. The liquor was then flashed further and diluted with water. Being insoluble in water, organosolv lignin precipitates in the dilution stage. The separated lignin was dried in spray driers.

After lignin separation, ethanol was recovered from the spent pulping liquor back to cooking by distillation. The distillation was carried out in two heat-integrated columns, with furfural recovered as a side draw. The furfural-rich side draw was further purified by phase separation and distillation. The bottoms stream from the two solvent (ethanol) recovery columns, containing hemicellulosic sugars and other compounds generated in the cooking and post hydrolysis, was evaporated in order to increase its solids content. Acetic acid, accumulating partially in the evaporator condensates, was recovered by extraction and purified by distillation. With the increase of solids content in the evaporation train, lower molecular weight (LMW) lignin not separated in the lignin precipitation stage was assumed to form an organic phase allowing its separation. After separation, the LMW lignin fraction was combusted in the boiler. After evaporation, the content of residual LMW compounds was further reduced by extraction, and the pH of the stream was conditioned by ammonia.

The sugars from the enzymatic hydrolysis of pulp and the hemicellulosic sugars were fermented to ethanol. The recovery and purification of the ethanol product was carried out in two distillation columns and molecular sieves. Steam and electricity were produced from both the residues of the process and additional fuel (natural gas).

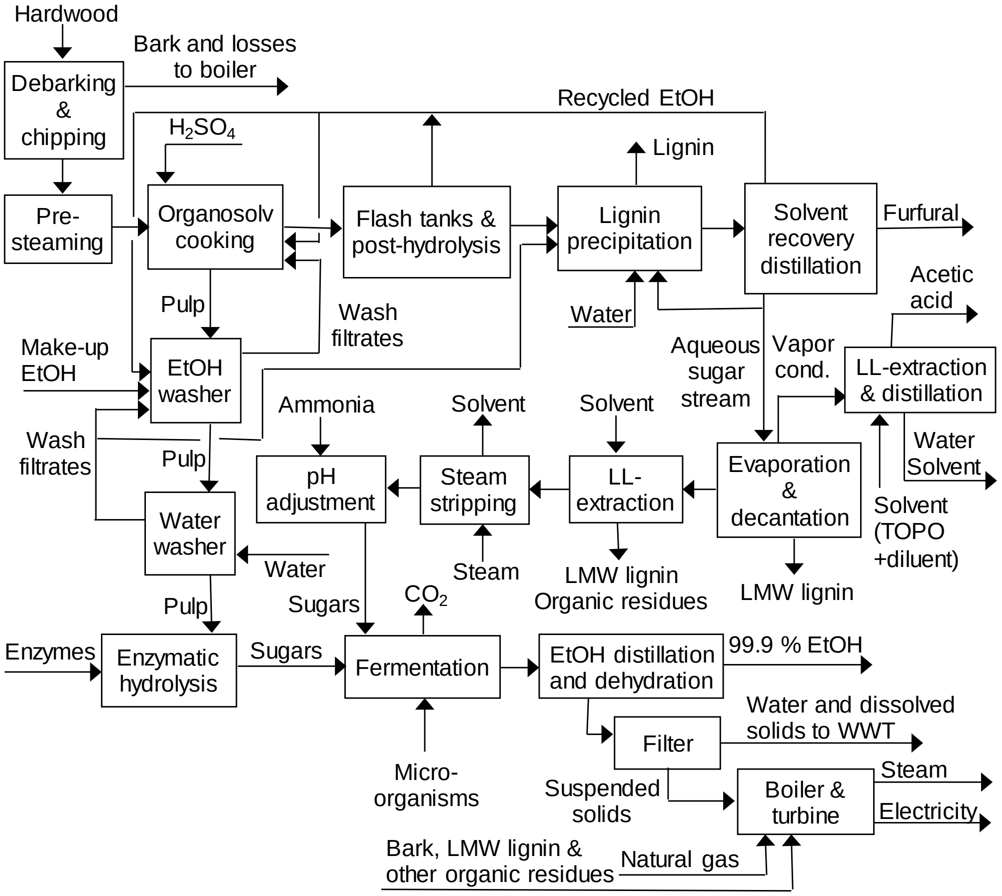


Figure 10: Block diagram of the modeled ethanol organosolv biorefinery (Kautto et al. 2013), (Biomass Conversion and Biorefinery, Design and simulation of an organosolv process for bioethanol production, 3(3), 2013, pp. 199-212, Kautto et al.,”With permission of Springer”).

Based on the developed conceptual process design and simulation model, mass and energy balances were compiled for the process. Table 15 below presents the main inputs and outputs of the organosolv process.

Table 15: The raw materials and products of the process (based on Kautto et al. 2013), (Biomass Conversion and Biorefinery, Design and simulation of an organosolv process for bioethanol production, 3(3), 2013, pp. 199-212, Kautto et al.,”With permission of Springer”).

| | Flow rate, t/d | | Flow rate, t/d |
|---|---|---|---|
| **Raw materials** | | External fuel (natural gas) | |
| Feedstock (dry) | | To boiler | 45.1 |
| Hardwood chips | 2000 | To lignin drying | 10.9 |
| Bark and debarking losses | 353 | | |
| Total feedstock | 2353 | **Products** | |
| Chemicals, enzyme and nutrients | | Ethanol | 459.1 |
| $H_2SO_4$ | 20.2 | Organosolv lignin | 310.5 |
| Ammonia | 12.4 | Furfural | 6.6 |
| Cellulase | 15.5 | Acetic acid | 30.3 |
| Corn steep liquor | 25.3 | Excess electricity | 87.0 MWh/d (3.6 MW) |
| Diammonium phosphate | 3.3 | | |

As presented in Table 15, the feedstock feed of 2000 Odt/d debarked wood chips resulted in the production of 459 t/d of ethanol (corresponding to 53.9 million gallons/204 million liters per year). This corresponded to a carbohydrate to ethanol conversion rate of 64 %, which was found to be lower than that in the reference, dilute acid pretreatment -based ethanol production process (76 %, based on Humbird et al. 2011). The rather big difference in the conversion rates between the organosolv study (Pan et al. 2006) and the NREL dilute acid study (Humbird et al. 2011) can be particularly due to differences in the experimental setups, raw materials and assumptions in the two studies. Also the relatively high temperature and high residence time in organosolv cooking, potentially leading to lower carbohydrate recovery in the pretreatment step, could partially explain the conversion rate difference. The actual difference in conversion rates could therefore well be lower than assumed in Publication III. The actual conversion rates would need to be tested experimentally with the same raw material in comparable conditions. Sensitivity analyses, studying the effect of improved conversion rate in enzymatic hydrolysis in the organosolv process (which has a similar effect on the MESP as improved carbohydrate recovery in pretreatment), were presented in Publication IV (see subsection 5.4).

The production rate of lignin was 310 t/d, being 67 % of the original lignin present in the wood chips. The production rates of other co-products, namely furfural (6.6 t/d) and acetic acid (30.3 t/d), were found to be considerably lower. With the recovery of the co-products, the total yield of the recovered products was approximately 40 % (defined here as the mass of products over the mass of dry wood chips), being considerably higher than in the reference dilute acid process (26 %, based on Humbird et al. 2011).

Due especially to the recovery of the solvent, the energy consumption of the process was found to be higher than in the reference dilute acid process. Along with the recovery of a relatively high share of the feedstock as products, this resulted in the demand of external fuel. A potential trade-off was therefore seen between the possibility of recovering multiple co-products, and especially pure lignin, in the organosolv process, and the higher carbohydrate to ethanol conversion and lower energy consumption of the dilute acid process. Furthermore, the increasing number of processing steps in the organosolv process was expected to increase the investment cost. This trade-off was examined further in Publication IV.

The main contribution of the third publication was the development of a conceptual process design and simulation model of the organosolv process for bioethanol production, including the recovery of co-products lignin, acetic acid and furfural. The organosolv process was compared to the reference dilute acid process in a systematic way, in order to understand the relative merits and drawbacks of the process better. With the development of the simulation model, detailed flowsheets and balance information were presented of the modeled process, providing a sound basis for an economic assessment of the process (presented in Publication IV).

## 5.4 Publication IV: Economic analysis of an organosolv process for bioethanol production

*Objective*

Based on the simulation model and flowsheets presented in Publication III, the main objective of the fourth publication was to assess the economic feasibility of the organosolv pulping -based bioethanol production process. Based on an analysis of the operating and investment costs and co-product revenues, the economic feasibility was quantified by the minimum price of the ethanol required to cover the costs of production and make a certain return on the invested capital (MESP). A further aim of the publication was to evaluate the effect of the recovery of co-products, as well as the effect of changes in the key technical and economic parameters, on the MESP. The economic feasibility of the process was also compared to that of the reference dilute acid pretreatment -based ethanol production process (based on Humbird et al. 2011), and the price of organosolv lignin required to make the organosolv process competitive was analyzed. The economic analysis in the publication was carried out in the 2013 value of the US dollar. Throughout the thesis the results of the economic analysis are therefore reported in 2013 dollars. The publication provided input to research questions *Q3* and *Q5*.

*Results and main contribution*

The investment cost of the studied organosolv process, producing 459 t/d of ethanol from 2000 Odt/d of debarked hardwood chips, was estimated to be approximately 720 million USD. Table 16 presents the breakdown of the investment cost.

Table 16: Investment cost analysis (based on Kautto et al. 2014).

| Investment cost | MUSD | Investment cost | MUSD |
|---|---|---|---|
| *Installed equipment cost* | | *Indirect costs* | |
| Process areas | | Prorateable expenses (10% of TDC) | 43 |
| Feed handling | 42 | | |
| Pretreatment and lignin recovery | 88 | Field expenses (10% of TDC) | 43 |
| Solvent and furfural recovery | 31 | | |
| Conditioning of the hemicellulosic stream | 19 | Home office and construction (20% of TDC) | 86 |
| Acetic acid recovery | 12 | Project contingency (10% of TDC) | 43 |
| Enzymatic hydrolysis and fermentation | 28 | Other costs (10% of TDC) | 43 |
| Ethanol product and solids fermentation | 18 | **Total indirect costs** | **257** |
| Wastewater treatment | 54 | | |
| Storages | 5 | **Fixed capital investment (FCI)** | **685** |
| Boiler and turbine | 82 | Land | 3 |
| Utilities | 7 | Working capital (5% of FCI) | 34 |
| **Total installed equipment cost** | **386** | | |
| *Other direct costs* | | **Total capital investment** | **722** |
| Warehouse (4% of ISBL) | 10 | | |
| Site development (9% of ISBL) | 21 | | |
| Additional piping (4.5% of ISBL) | 11 | | |
| **Total direct costs (TDC)** | **428** | | |

Indexed to 2013 dollars, the total capital investment of an equally sized dilute acid pretreatment -based bioethanol production process (based on Humbird et al. 2011) was found to be approximately 460 MUSD. Not unexpectedly, the more complex flowsheet of the organosolv process, with the recovery of the solvent and co-products, resulted in a higher investment cost.

The variable and fixed operating costs were calculated to be approximately 130 million USD/year and the revenues from co-products approximately 61 million USD/year, which along with the investment cost, resulted in minimum ethanol sales of 166 million USD/year. This corresponded to a minimum ethanol sales price of 3.07 USD/gal (0.81 USD/L, 1030 USD/t). Table 17 below presents the breakdown of the MESP calculation per gallon of ethanol produced.

Table 17: Breakdown of the MESP of the organosolv process to cost contributors (adapted from Kautto et al. 2014).

| Cost contributor | USD/gal | USD/L |
|---|---|---|
| Feedstock | 1.30 | 0.34 |
| Enzyme | 0.53 | 0.14 |
| Other chemicals & ash disposal | 0.17 | 0.05 |
| Natural gas | 0.08 | 0.02 |
| Co-products | | |
| Organosolv lignin | -0.91 | -0.24 |
| Furfural | -0.07 | -0.02 |
| Acetic acid | -0.12 | -0.03 |
| Electricity | -0.03 | -0.01 |
| Fixed costs | 0.32 | 0.08 |
| Capital depreciation | 0.42 | 0.11 |
| Tax | 0.24 | 0.06 |
| Average return on investment | 1.14 | 0.30 |
| **Total** | **3.07** | **0.81** |

As can be seen in Table 17, the feedstock (with a delivered price of 85 USD/Odt) and enzyme costs (price and dosage of 5270 USD/t and 0.02 g/g cellulose), the lignin co-product credit (at a base case lignin price of 450 USD/t), and the capital costs were found to be the major cost factors in the production of cellulosic ethanol through the organosolv process. Aligning the feedstock costs of the reference dilute acid bioethanol process (Humbird et al. 2011) with the cost used in evaluating the feasibility of the organosolv process and indexing other operating costs and investment costs to the cost year of the organosolv study (2013) resulted in an MESP of 2.6 USD/gal (0.69 USD/L, 870 USD/t), being somewhat lower than the MESP of the organosolv process. This showed that organosolv pretreatment for the production of bioethanol could be competitive, with either a slightly higher price of lignin than the base case price of 450 USD/t, or lower investment or operating costs.

Sensitivity analyses were run to study the economic feasibility of the organosolv process further. Table 18 shows the effect of changes in the studied technical parameters, as well as the investment cost and discount rate on the MESP. The effects of lignin sales price and feedstock and enzyme costs on the MESP are shown separately in Figure 11.

Table 18: Sensitivity of MESP to technical parameters, investment cost and discount rate (adapted from Kautto et al. 2014). One gallon converts to 3.79 liters.

| Design parameter | Base case | Value in sensitivity analysis | MESP, USD/gal |
|---|---|---|---|
| Steam and power consumption | 6720 t/day (steam),<br>670 MWh/day (power) | 8740 t/day,<br>870 MWh/day (+30%)<br>4710 t/day,<br>470 MWh/day (-30%) | 3.25 (+0.18)<br>2.91 (-0.17) |
| Conversion rate in enzymatic hydrolysis | 90% for cellulose,<br>82% for hemicelluloses | 96% for cellulose, 88% for hemicelluloses (high)<br>80% for cellulose and hemicelluloses (low) | 2.92 (-0.15)<br>3.38 (0.30) |
| Conversion rate of hemicellulosic sugars in fermentation | 85% for C5 sugars, 0% for C6 sugars | 85% for C5 and C6 sugars (high)<br>50% for C5 sugars, 0% for C6 sugars (low) | 2.88 (-0.19)<br>3.23 (0.16) |
| Total capital investment | 722 MUSD | 939 MUSD (+30%)<br>505 MUSD (-30%) | 3.60 (+0.53)<br>2.54 (-0.53) |
| Discount rate used in MESP calculation | 10 % | 20 % | 4.30 (+1.23) |

As can be seen in the table, the MESP was very sensitive to changes in investment costs, with 30 % decrease in the investment cost decreasing the MESP by 0.53 USD/gal (0.14 USD/L, 180 USD/t). Instead of constructing a greenfield plant, the investment cost could be possibly lowered by integrating the plant into an existing industrial site or facility with for example existing utility systems. Additional capital savings could be possibly found in simplifying the process, for example by omitting the construction of the acetic acid recovery process, which was found to have a relatively long payback period. Also the conversion rates in both enzymatic hydrolysis and fermentation had a rather considerable effect on the MESP, highlighting the importance of the overall conversion rate from carbohydrates to ethanol in the economics of the process concept.

Possibly the largest source of uncertainty in the economic analysis of the organosolv process is the price of the organosolv lignin. A wide scale of various uses could be assumed for the lignin, ranging from using it in energy production to very high-value applications, such as carbon fibers. Especially various resin systems, such as phenol-formaldehyde resins, have been suggested for organosolv lignin. To study the effect of the price of lignin on the MESP of the process, the price was varied within a price range, with its value as energy (based on the price of coal) as the minimum price and the price of phenol as the maximum. Figure 11 presents the results of this analysis. It should be noted that the reference phenol price in the figure is from February 2013. The price of phenol is volatile, and has decreased along with the decreasing oil price. It should furthermore be kept in mind that lignin needs to be processed before it can be used as a phenol replacement. Therefore, the price of phenol in the figure below represents only a very optimistic upper end of the lignin price range, not a realistic value of lignin as a phenol replacement.

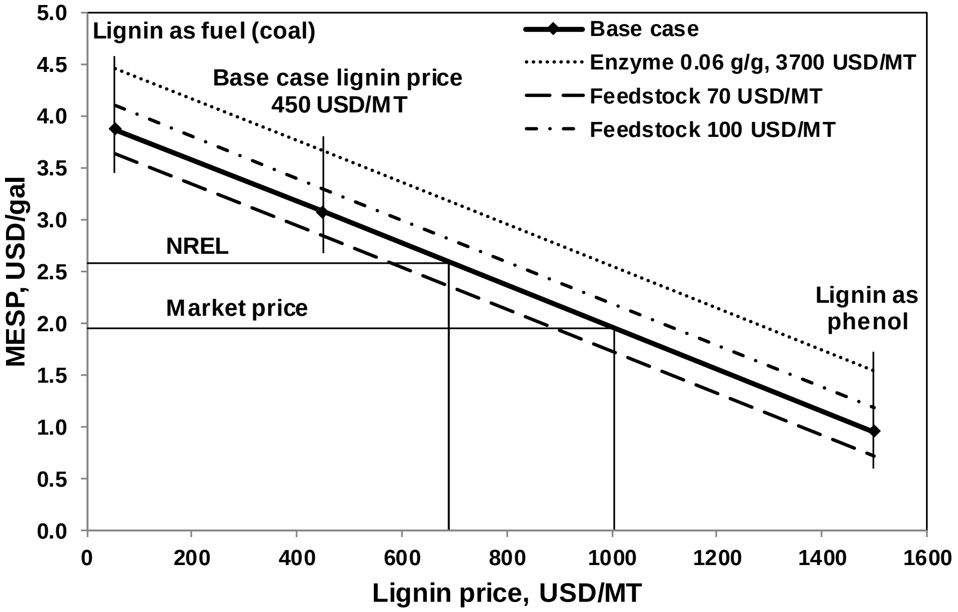


Figure 11: The effect of the selling price of lignin on the MESP of the organosolv process. Market price in the figure refers to the December 2013 market price of ethanol (Chicago Mercantile Exchange 2013) and NREL to the MESP of the reference dilute acid process (Humbird et al. 2011), indexed to 2013 and feedstock cost adjusted. The figure also presents the effect of enzyme and feedstock costs on the MESP (Kautto et al. 2014). One gallon converts to 3.79 liters. MT in the figure refers to metric tons.

As can be seen in the figure, the MESP of the organosolv process was sensitive to changes in the price of lignin. The very optimistic upper end of the lignin price range, lignin sold at the February 2013 price of phenol resulted in an MESP that was slightly below 1.0 USD/gal (0.25 USD/L, 320 USD/t), making the organosolv biorefinery concept economically very promising and cost competitive against the dilute acid process (MESP 2.6 USD/gal (0.69 USD/L, 870 USD/t), with feedstock cost aligned and other costs indexed to 2013). At lignin sold in turn at its coal-based fuel value, the MESP was considerably higher (3.9 USD/gal, 1.0 USD/L, 1300 USD/t) than that of the dilute acid process, clearly indicating that higher-valued applications than combustion would need to be found for lignin for the organosolv process to be economically competitive. The price of lignin corresponding to the MESP of the dilute acid process was 690 USD/t. In addition to lignin, Figure 11 presents also the relatively high sensitivity of the MESP to variations in feedstock and enzyme costs, highlighting the significance of enzyme development and securing of low-cost feedstock in the viability of this or any other enzymatic lignocellulosic ethanol production process.

The main contribution of Publication IV was the comprehensive economic evaluation of the organosolv process. The operating and investment costs of the process were evaluated and the cost competitiveness of the process was compared to the dilute acid process in a systematic way. While Publication III identified a number of advantages and disadvantages of the organosolv process, Publication IV evaluated these in numerical, economic terms.

## 5.5 Summary of the publications

The objective of the thesis was to evaluate the conceptual feasibility of two biorefinery concepts: co-production of pulp and bioethanol, based on the extraction of hemicelluloses from wood chips prior to kraft pulping and organosolv pulping for the fractionation of biomass and production of bioethanol. The thesis consists of four research articles, which are summarized in the table below.

Table 19: A summary of the publications in the thesis.

| | Publication I | Publication II | Publication III | Publication IV |
|---|---|---|---|---|
| Title | Effects of integrating a bioethanol production process to a kraft pulp mill | Digestibility and paper-making properties of prehydrolyzed softwood chips | Design and simulation of an organosolv process for bioethanol production | Economic analysis of an organosolv process for bioethanol production |
| Objective | Development of a simulation model, establishing balances over the pulp and ethanol producing process | Evaluation of the effect of hemicellulose extraction on pulping and pulp quality | Development of a conceptual process design and simulation model of the organosolv process | Evaluation of the economic feasibility of the organosolv process |
| Research question | *Q1, Q2* | *Q2* | *Q3, Q4* | *Q3, Q5* |
| Method | Process simulation | Experimental work | Process simulation | Economic evaluation |
| Data | Experimental data, additional input from literature and industry | Experimental data, additional input from literature | Literature | Simulation model, with input from industry and literature |
| Main results | At a pulp mill producing 1000 Adt/t of pulp, hemicellulose extraction prior to kraft pulping resulted in ethanol production of 40 t/d, wood consumption increase of 16 %. and various effects on the pulp mill fiberline and chemical recovery. | Water prehydrolyzed wood chips required a reduced cooking time, and the pulp responded well to $O_2$ delignification and required less bleaching chemicals than the reference. The tensile index decreased and the tear index increased, while the beating response deteriorated considerably. | Hardwood feed of 2350 Odt/d resulted in ethanol production of 459 t/d. The carbohydrate to ethanol conversion was lower and the energy consumption higher than in the reference process. With the recovery of co-products lignin, furfural and acetic acid, the total yield of recovered products was, however, higher. | The price of lignin contributed considerably to the MESP of the organosolv process. With a base case lignin price of 450 USD/t, the MESP was 3.1 USD/gallon (0.81 USD/L, 1030 USD/t), being higher than that of the reference process. A higher lignin price of 690 USD/t was required to make the organosolv process cost competitive with the reference. |

## 5.6 Research findings

Subchapters 5.6.1 and 5.6.2 below outline briefly the answers to the research questions *Q1 – Q5* of this thesis. The main research question is discussed in Chapter 6.

### 5.6.1 Hemicellulose extraction (research questions Q1 – Q2)

Two research questions were outlined concerning the hemicellulose extraction concept. These two questions are discussed below.

*Q1: What is the overall process concept for hemicellulose extraction -based ethanol production and what are the mass balances over hemicellulose extraction and cooking, as well as ethanol production?*

Publication I outlined the hemicellulose extraction-based ethanol production concept assumed in this thesis. In the process, hot water at 150 °C for 1 h 41 min was used to dissolve the hemicelluloses. The generated prehydrolyzate was then drained from the prehydrolysis reactor and fed to downstream processing. With an assumed liquor-to-wood ratio of 4:0 L/kg in the prehydrolysis reactor, 60 % of the prehydrolyzate was assumed to be recovered and 40 % to remain in the wood pores.

In the laboratory experiments described in the publication, the temperature and time in water prehydrolysis presented above were found to dissolve 14.1 % of the original dry wood material, 6.8 % being hemicelluloses and the rest other wood components (including acetic acid, lignin and extractives). The dissolved carbohydrates (primarily hemicelluloses) were mainly in an oligomeric form. The prehydrolyzate was further found to contain two phases, dissolved material and a precipitate.

After drainage, the prehydrolyzate was assumed to be flashed, followed by mechanical separation (e.g. centrifugation) to separate the precipitate and mild acid hydrolysis (post hydrolysis) to convert the oligomers to monomeric sugars. The prehydrolyzate was then assumed to be fed to a liming stage, where the sulfuric acid used in mild acid hydrolysis was precipitated as calcium sulfate ($CaSO_4$) by using calcium oxide (CaO). To increase its solids content, the neutralized prehydrolyzate was then evaporated in evaporation effects that were heat-integrated with the black liquor evaporation plant. The prehydrolyzate was then fed to fermentation, where 90 % of pentose and hexose sugars were assumed to be converted to ethanol. The produced ethanol was assumed to be recovered by distillation and molecular sieves. Figure 12 below is a block diagram of the studied hemicellulose extraction -based pulp and ethanol -producing biorefinery.

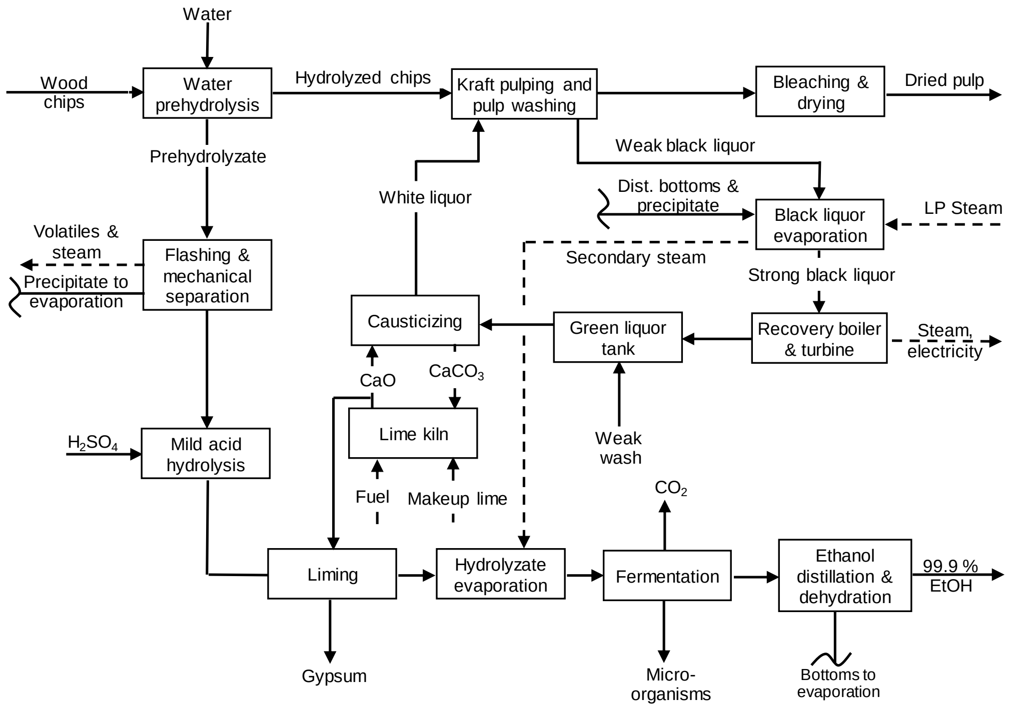


Figure 12: Studied hemicellulose extraction -based pulp and ethanol -producing biorefinery (adapted from Kautto et al. 2010a).

In the cooking experiments, the yields on wood after cooking and oxygen delignification were 40 % and 38.5 %, respectively, for prehydrolyzed wood chips. In the reference case, with no hemicellulose extraction, the respective yields were 46.2 % and 44.7 %. In the study, pulp production was assumed to be kept constant at 1 000 Adt/d. The yield decrease resulted in a wood consumption increase of 16 %, from 2327 to 2703 oven dry tons (Odt)/d of undebarked wood. The extraction of 14.1 % of wood material in the water prehydrolysis stage resulted in the production of 40 t/d of ethanol. Figure 13 below summarizes the dry solids mass balances presented in Publication I over the hemicellulose extraction -based pulp and ethanol -producing biorefinery and the reference, a conventional pulp mill.

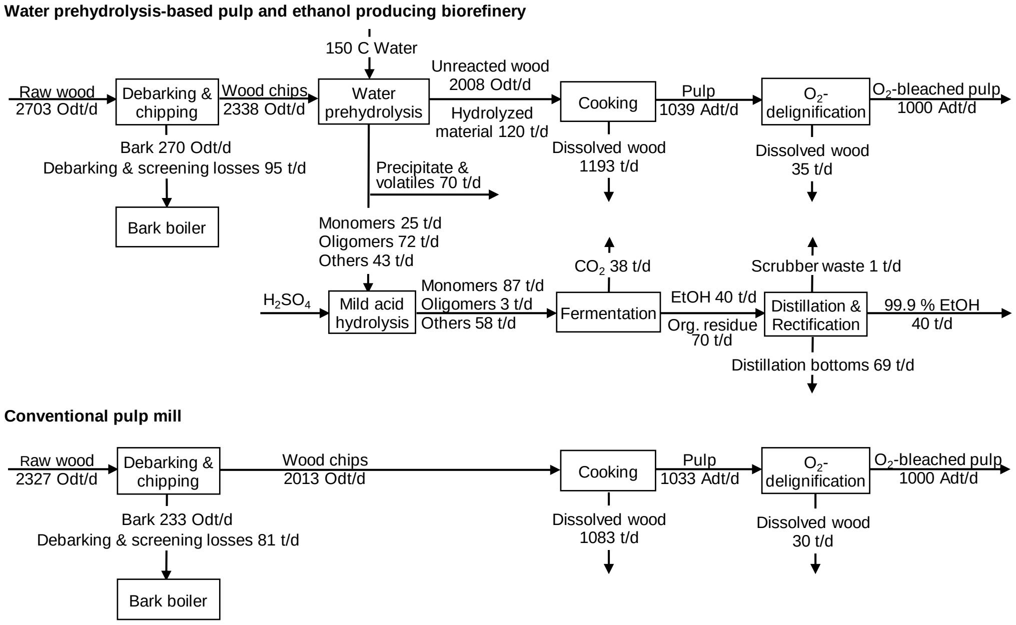


Figure 13: Tentative dry solids mass balances over a hemicellulose extraction -based pulp and ethanol -producing biorefinery and a conventional pulp mill (adapted from Kautto et al. 2010).

*Q2: What is the effect of hemicellulose extraction on the pulp mill fiberline, chemical recovery and the quality of the produced pulp?*

The second research question was addressed in Publications I and II. The effects on the pulp mill fiberline were discussed in both publications, while Publication I addressed chemical recovery and Publication II the quality of the produced pulp.

Concerning the pulp mill fiberline, it was found in Publication I that water prehydrolysis decreased the yield on wood considerably. This would increase the load on the debarking and chipping equipment and the bark boiler. In cooking, a lower H-factor was required in the cooking of prehydrolyzed chips, indicating that either a shorter cooking time or a lower temperature would be required to obtain a given kappa number. The effects of water prehydrolysis on the yield and H-factor were confirmed in Publication II. It was found further in Publication II that water prehydrolysis increased the degree of delignification in the $O_2$ stage and decreased the amount of bleaching chemicals required to obtain a given brightness.

In chemical recovery, Publication I identified the key effects of hemicellulose extraction to take place in the evaporation plant and the recovery boiler. The load in these two mill areas was found to be increased due to the increased amount of organics and water entering the chemical recovery cycle, increased heating value of the black liquor, and the coupling of the evaporation of the prehydrolyzate with the black liquor evaporation plant. Although the steam consumption increased, the increased load on the bark and recovery boilers increased the electricity generation of the mill. The rest of the chemical recovery cycle was found to be largely unaffected.

Concerning the quality of the pulp, in Publication II the key effects were found to be a considerable decrease in the beating response, as well as a decrease in the tensile index and an increase in the tear index.

### 5.6.2 Organosolv process (research questions Q3 – Q5)

Three research questions were outlined concerning the organosolv process. These questions are discussed below.

*Q3: What is the overall process concept for an organosolv pulping -based biorefinery, including pulping, ethanol production and the recovery of by-products? How can the process be compared systematically to the more standard dilute acid pretreatment -based lignocellulosic ethanol production?*

The organosolv concept for bioethanol production was outlined in Publication III, and summarized in subchapter 5.3 above. In the studied process concept, hardwood chips were first delignified in organosolv cooking, followed by washing and enzymatic conversion of the produced pulp to sugars. The sugars were then fermented to ethanol, followed by recovery and purification by two distillation columns and molecular sieves.

The spent cooking liquor was first flashed for solvent and heat recovery, followed by a post-hydrolysis step to convert oligomers to monomers. The liquor was then flashed further and diluted with water to precipitate and recover lignin. After lignin separation, ethanol was recovered from the spent pulping liquor by distillation. Furfural was recovered from the distillation columns as a side draw. The bottoms stream from the distillation columns was evaporated to increase its solid content, with acetic acid recovered from the evaporator condensates by extraction and purified by distillation. Also lower molecular weight lignin was assumed to be separated in the evaporation stage. This lignin fraction was assumed to be combusted. After evaporation, the stream containing hemicellulosic sugars was further purified and conditioned by extraction and ammonia addition, followed by fermentation to ethanol together with the sugars produced from the pulp stream.

A conceptual process design and simulation model for the studied process concept was developed on the basis of literature data. The NREL report (Humbird et al. 2011) on the dilute acid pretreatment -based ethanol production was used as a benchmark study. To the extent applicable, the report was also used to create the models of the process sections downstream of organosolv pulping and the recovery of solvent and co-products, that is enzymatic hydrolysis, fermentation and ethanol recovery and purification, as well as auxiliary processes. In addition to the parameters within these downstream and auxiliary processes, also the rate of dry feedstock intake to the process was set according to the NREL study. The economic evaluation of the organosolv process (presented in Publication IV), which was built based on the conceptual process design and simulation model, followed the NREL study closely as well. This enabled justifiable technical and economic comparisons of the organosolv and dilute acid processes.

*Q4: What are the mass and energy balances of the organosolv process and how does the process compare technically to the dilute acid process?*

The mass and energy balances of the organosolv process and the technical differences compared to the dilute acid process were discussed in Publication III and summarized in subchapter 5.3 above. In the studied organosolv concept, the feedstock intake was 2350 Odt/d of undebarked wood, which resulted in 2000 Odt/d of debarked chips fed to organosolv cooking. The production rate of ethanol was 459 t/d (53.9 million gallons/204 million liters per year), which corresponded to a carbohydrate to ethanol conversion rate of 64 %. This conversion rate was lower than with the reference, dilute acid pretreatment -based ethanol production process (76 %, based on Humbird et al. 2011). The production rates of co-products, namely organosolv lignin, furfural and acetic acid, were 310, 7 and 30 t/d, respectively. Although the ethanol yield was lower in the organosolv process, the recovery of co-products resulted in a higher total yield of recovered products (approximately 40 %) compared to the dilute acid process (26 %, based on Humbird et al. 2011).

Due to particularly the recovery of the solvent, the energy consumption of the process was found to be 34 % higher than that of the reference dilute acid process. The higher energy consumption and higher total yield of recovered products of the organosolv process resulted in a need of external fuel (natural gas). A total of 56 t/d (778 MWh/d, 32 MW) of natural gas was required to cover the steam demand of the process and to dry the recovered organosolv lignin. A small amount of excess electricity (87 MWh/d, 4 MW) was produced concurrently.

As a summary, a trade-off was found between the recovery of co-products in the organosolv process and its lower ethanol yield and the higher energy consumption compared to the dilute acid process.

*Q5: What is the economic feasibility of the organosolv process for bioethanol production? How does it compare economically to the dilute acid pretreatment -based ethanol production process?*

The economics of the organosolv process were discussed in Publication IV and summarized in subchapter 5.4 above. The economic assessment was carried out based on the simulation model and flowsheets presented in Publication III. MESP was used to quantify the economic feasibility of the process and compare it to the reference dilute acid pretreatment -based ethanol production process (based on Humbird et al. 2011).

The investment cost of the studied organosolv process, producing 459 t/d of ethanol, was estimated to be approximately 720 million USD. The variable and fixed operating costs were in turn approximately 130 million USD/year and revenues from co-products, at a base case lignin price of 450 USD/t, 61 million USD/year. These resulted in minimum ethanol sales of 166 million USD/year, corresponding to a minimum ethanol sales price of 3.1 USD/gal (0.81 USD/L, 1030 USD/t). The reference dilute acid process had a lower investment cost (approximately 460 million USD) and MESP (2.6 USD/gal, 0.69 USD/L, 870 USD/t). The organosolv process was therefore not economically competitive with the dilute acid process at the base case lignin price. In sensitivity analyses it was found that a higher lignin price of 690 USD/t was required to bring the MESP of the organosolv process at the same level as that of the dilute acid process.

# 6 Discussion

In this chapter, the findings of the study are summarized and the main research question addressed. The main theoretical contributions, practical implications, limitations and suggestions for further research are then discussed. Prior to these, the load increases in the evaporation plant and recovery boiler presented in Publication I are discussed.

## 6.1 Revisit to Publication I, load increases in the evaporation plant and recovery boiler

In Publication I, hemicellulose extraction was found to result in considerable capacity increases in the evaporation plant and recovery boiler. Concerning these effects, it should be noted that a number of assumptions made during the construction of the simulation model impacted them considerably. These assumptions, as well as how adjustments in them could result in less pronounced effects, are discussed below.

Firstly, all residues originating in water prehydrolysis were assumed to be combusted in the recovery boiler. This increased the heat load considerably. The residues could be combusted possibly more suitably in a separate biomass boiler or partly also in the bark boiler, off-loading the recovery boiler. Simultaneously, also the load on the evaporation plant would be decreased. In addition to the combustion of residues, the load increase on the recovery boiler was also based on an increase in the heating value of black liquor. Based on laboratory experiments, water prehydrolysis increased the heating value of black liquor by 0.7 MJ/kg. Due to the small scale of the experiments and the combining of data from two separate sets of experiments in the simulation model (see subchapter 4.5.1, experiments carried out at the University of Jyväskylä and Helsinki University of Technology), there is uncertainty in the exact amount of heating value increase. Hamaguchi et al. (2013) calculated a heating value difference of 0.5 MJ/kg based on the same mass balance over hemicellulose extraction and cooking that was presented in Publication I. This indicates that the heating value increase adopted in the simulation model might have been too pronounced. Adopting the same heating value increase as Hamaguchi et al. (2013) and assuming no combustion of prehydrolyzate residues in the recovery boiler, the effects on the recovery boiler would be similar to those calculated by Hamaguchi et al. (2013), with hemicellulose extraction increasing steam generation by 13.5 %.

Regarding the evaporation plant, the water contained in wood chip pores after hemicellulose extraction, the evaporation and combustion of prehydrolyzate residues in the recovery boiler, and coupling of the prehydrolyzate evaporation to black liquor evaporation increased the steam consumption and required heat transfer areas. As discussed above, the assumption of combusting the prehydrolyzate residues in the recovery boiler could be well forgone. Also assumptions related to the coupling of black liquor and prehydrolyzate evaporation could have a considerable effect on the load to the evaporation plant. In the simulation model, the pressure of the steam withdrawn from the final effect (effect 7 in the reference case and effect 9 in the hemicellulose extraction case) was kept constant at 15 kPa. This increased the required heat transfer areas unnecessarily. An assumption leading to lower overall heat transfer areas would be to maintain the pressure after effect 7 at 15 kPa (in other words, to keep the process parameters in the black liquor side of the evaporation unchanged) and decrease it further in effects 8 and 9. Alternatively, the concentration of the prehydrolyzate could be forgone completely or carried out by using some alternative technology, such as reverse osmosis (Mao et al. 2010). Assuming no feeding of the prehydrolyzate residues to the evaporation plant and no coupling of black liquor evaporation to prehydrolyzate evaporation, the amount of water evaporated in the hemicellulose extraction case would have increased by 12 %.

As is evident from the discussion above, the effects of water prehydrolysis on the load increases in the recovery boiler and evaporation plant could be somewhat lower than those presented in Publication I. The revised load increases are, however, still considerable, and would lead to sizable increases in investment costs, which would then have an effect on the economic feasibility of the concept. The discussion of the viability of the process concept presented in subchapter 6.2.1 is therefore valid, regardless of whether these revised load increases or the original increases presented in Publication I are adopted.

## 6.2 Summary of the findings and the main research question

The research questions *Q1 – Q5* were addressed in Chapter 5. These are first briefly summarized in this subchapter, followed by addressing the main research question.

The process concept for hemicellulose extraction-based co-production of paper-grade pulp and ethanol studied in this thesis consisted of hot water prehydrolysis at 150 °C for 1 h 41 min. In laboratory experiments these conditions were found to dissolve 14.1 % of the original dry wood material, 6.8 % being hemicelluloses. The generated prehydrolyzate, containing the dissolved organic material, was first drained and flashed, followed by mechanical separation, mild acid hydrolysis, liming, evaporation, fermentation and ethanol recovery. The hemicellulose extraction decreased the yield on wood after oxygen delignification considerably, from 44.7 % to 38.5 %. With constant pulp production at 1000 Adt/d, this increased wood consumption by 16 %. The extraction of 14.1 % of wood in the prehydrolysis stage resulted in a relatively low ethanol output of 40 t/d (*Q1*).

The decrease in the yield on wood increased the load on the debarking and chipping equipment and the bark boiler. Other effects of hemicellulose extraction on the pulp mill fiberline were found to be a lower H-factor in cooking, an increased degree of delignification in the $O_2$ stage, and a decrease in the required amount of bleaching chemicals. The key effects in the chemical recovery were an increased load in the evaporation plant and the recovery boiler. The electricity generation of the mill was also increased. In terms of the quality of the pulp, the major effects of hemicellulose extraction were a decrease in the tensile index and an increase in the tear index (*Q2*).

In the organosolv process concept studied in this thesis, hardwood chips were cooked in a mixture of ethanol, water and sulfuric acid (catalyst). The produced pulp was washed and converted to sugars enzymatically. The spent cooking liquor was fed to a number of processing steps, including the post-hydrolysis stage, dilution with water to recover lignin, distillation to recover ethanol and furfural as a side-straw, evaporation, as well as purification and conditioning. The sugars from both the pulp and cooking liquor streams were assumed to be fermented to ethanol. The NREL report on dilute acid pretreatment – based ethanol production process (Humbird et al. 2011) was used both as a design basis and benchmark. This enabled systematic comparison of the two processes (*Q3*).

The studied process was assumed to have a feedstock intake of 2350 Odt/d of undebarked wood, which, after debarking and chipping, resulted in 2000 Odt/d of chips fed to organosolv cooking. The production rates of ethanol, organosolv lignin, furfural and acetic acid were 459, 310, 7 and 30 t/d, respectively. Compared to the dilute acid process, the ethanol yield of the organosolv process was lower, but the recovery of co-products resulted in a higher total yield of recovered products. The organosolv process was found to have a higher energy consumption, which, combined with the high total yield of recovered products, resulted in a need of external fuel (natural gas) (*Q4*).

The investment cost of the organosolv process was estimated to be approximately 720 million USD, while the minimum ethanol sales price (MESP) was 3.1 USD/gal (0.81 USD/L, 1030 USD/t) at a base case lignin price of 450 USD/t. The reference dilute acid process had lower investment cost and MESP, indicating that the organosolv process was not economically competitive with the dilute acid process at the base case lignin price. A higher lignin price of 690 USD/t was required to lower the MESP of the organosolv process to the same level as that of the dilute acid process.

Following the above summary of the research questions *Q1 – Q5*, the main research question rises:

*Are the two studied processes (pre-extraction of hemicelluloses prior to kraft pulping and organosolv pulping) feasible biomass fractionation and biorefinery concepts?*

The main research question is addressed below in separate sections for the two studied processes.

### 6.2.1 Conceptual feasibility of hemicellulose pre-extraction prior to kraft pulping

As presented in the review of Publications I and II (subchapters 5.1 and 5.2), in research question *Q2* (subchapter 5.6.1) and in the literature review (subchapter 3.1), the extraction of hemicelluloses from wood chips prior to kraft pulping has multiple effects on the operation of the pulp mill and on the quality of the pulp. Table 20 presents the main advantages and disadvantages of hemicellulose extraction through water prehydrolysis.

In addition to its effects on pulp mill operation and pulp quality, also the production of ethanol is taken into account in the table.

Table 20: Key advantages and disadvantages of hemicellulose extraction through water prehydrolysis prior to kraft pulping for the production of ethanol.

| Property | Advantages | Disadvantages |
|---|---|---|
| **Pulp mill operation** | | |
| Yield on wood | | Yield on wood decreases considerably. To maintain constant pulp production, in Publications I and II, wood consumption was found to increase by 16 % and 17 %, respectively. |
| Digester yield | | The effect of water prehydrolysis on digester yield varies between different studies but has generally been found to decrease (a slight increase was found in Publication I, however). Decreased digester yield increases the amount of organics entering chemical recovery. |
| Digestability and bleachability | Digestability (lower H-factor required in cooking) and response to $O_2$ delignification and bleaching are improved. | |
| Load on chemical recovery | | With constant pulp production, the load on the evaporation plant and recovery boiler increases considerably. Decreased digester yield could furthermore lead to increased load on the recaustizing plant and the lime kiln. |
| **Pulp quality** | | |
| Beating response | | Decreased hemicellulose content decreases the beating response considerably. In Publication II, water prehydrolyzed pulps were found to require several times more beating. |

| | | |
|---|---|---|
| Tensile strength | | Tensile strength decreases. |
| Tear strength | Tear strength increases. | |
| **Ethanol production** | | |
| Expansion of the product portfolio of the pulp mill | Water prehydrolysis enables the production of novel products (in this case ethanol) at pulp mills | |
| Processability of the prehydrolyzate | | Both the formation of sticky precipitates and the fermentability (due to inhibitors and C5 sugar content) and very low carbohydrate concentration of the prehydrolyzate are disadvantages. |
| Scale of production | | The ethanol output is relatively low. In Publication I, water prehydrolysis in a 1 000 Adt/d pulp mill resulted in ethanol production of 40 t/d. |

As discussed in subchapter 3.1.1, a majority of hemicelluloses are dissolved in conventional kraft cooking, followed by their combustion in a recovery boiler. As these hemicelluloses have a relatively low heating value, recovering them partially prior to pulping and converting them to value-added products could in principle offer an economic opportunity. This was the background in the BiSe project (2007 – 2010) in which the thesis work related to hemicellulose extraction was carried out primarily in 2009 – 2010. In an ideal process concept, the hemicellulose extraction stage would extract hemicelluloses that would otherwise be dissolved in cooking, while simultaneously having no effect on hemicelluloses that are retained in conventional cooking. At constant pulp production, such an ideal extraction concept would therefore result in low or no increase in wood consumption and an increased digester yield.

As is evident from Publications I and II and the literature review presented in subchapter 3.1, water prehydrolysis is far from an ideal extraction concept. The overall yield on wood decreases considerably, which in constant pulp production results in significant increase in wood consumption. In most studies, also the digester yield has been found to decrease, which is one reason increasing the load on chemical recovery. Concerning the effects of water prehydrolysis on the pulp mill, the increased wood consumption and the load on chemical recovery are two major disadvantages (see Table 20 above). The increased load on the evaporation plant and recovery boiler would lead to increased investment cost for the paper-grade pulp and ethanol -producing biorefinery.

In addition to the effects of water prehydrolysis on pulp mill operation, several disadvantages are furthermore related to the production of ethanol from the separated prehydrolyzate. Compared to an ethanol-only process (i.e. no pulp production, with all carbohydrates intended for ethanol production), the lower ethanol production capacity of the paper-grade pulp and ethanol -producing biorefinery results in higher specific (per unit of ethanol produced) capital costs. The other disadvantages of water prehydrolysis - based ethanol production include the low concentration of the prehydrolyzate (which will increase the processing costs) and its difficult processability (see Table 20 above). Furthermore, in the case of decreased digester yield and/or incomplete recovery of the prehydrolyzate, the biomass-to-ethanol yield (defined here as the ethanol output relative to the increase in the consumption of (debarked) wood) can be expected to be lower than in an ethanol-only plant. With a wood consumption increase of 325 dry t/d (from 2013 to 2338 dry t/d of wood chips, see Figure 13) in Publication I, the ethanol output is 40 t/d. This corresponds to a biomass-to-ethanol yield of approximately 13 %. The corresponding yield in the study of Humbird et al. (2011) (termed total yield of recovered products in subchapter 5.3) is considerably higher at 26 %. In addition to a lower yield, the studied paper-grade pulp and ethanol producing biorefinery may also have a raw material cost disadvantage. While the exact cost depends on the region and exact type of raw materials, the paper and pulp -producing biorefinery requires potentially more valuable raw material than an ethanol-only plant (pulp wood compared to e.g. agricultural residues).

In a pulp mill biorefinery producing 1000 Adt/d of pulp, the ethanol production was found to be only 40 t/d (Publication I). It is therefore evident that the main product of the process concept is pulp, and the attractiveness of the concept is to a considerable extent dictated by the effects of the extraction on the quality of the pulp. The disadvantages related to the effects of hemicellulose extraction on pulp mill operation and to the processing of the prehydrolyzate to ethanol could therefore be potentially offset if the extraction were beneficial for the quality of the produced pulp. As indicated in Table 20 above (and in closer detail in Table 5 in subchapter 3.1.2), water prehydrolysis cannot in general be expected to improve the properties of pulp. The work carried out in this thesis, including both Publications I and II and the literature review, indicates therefore that water prehydrolysis for the co-production of general, bulk-type paper-grade pulp and ethanol cannot be considered as attractive process concept. As indicated also by Saukkonen (2014), a specialty, higher value end-use, benefiting from the specific properties of hemicellulose extracted pulp, would be required for the produced pulp for the process concept to be more attractive. While being outside the scope of this thesis (co-production of paper-grade pulp and ethanol), it should be kept in mind that the specialty type of pulp currently produced through prehydrolysis and kraft pulping is dissolving pulp (see subchapter 3.1.1).

As a conclusion, it can be stated that based on the research carried out in this thesis, water prehydrolysis for the co-production of paper-grade pulp and ethanol cannot in general be considered to be an attractive process concept. A specialty type of pulp application, benefiting from the properties of water prehydrolyzed pulp, would need to be identified to improve the viability of the process concept. Process improvements that would increase the selectivity of the extraction and cooking steps considerably, bringing the process closer to the abovementioned ideal extraction concept by generating hemicelluloses at higher concentration and purity and increasing the digester yield, would furthermore improve the attractiveness of the process concept.

### 6.2.2 Conceptual feasibility of organosolv pulping

The key differences between the studied organosolv pulping and the reference dilute acid pretreatment -based ethanol production process were highlighted in the review of Publications III and IV (subchapters 5.3 and 5.4) and in research questions *Q4* and *Q5* (5.6.2). Similarly to the evaluation of the hemicellulose extraction concept (6.2.1), the technical differences are listed in Table 21 below as advantages and disadvantages of the organosolv concept.

Table 21: Key technical advantages and disadvantages of organosolv pulping for the production of ethanol (as compared to dilute acid pretreatment -based ethanol production).

| Property | Advantages | Disadvantages |
|---|---|---|
| Recovery of co-products | The key advantage of the organosolv process is the ability to recover co-products, particularly organosolv lignin. In addition to lignin, the process concept presented in Publication III recovered also furfural and acetic acid. With these co-products, a higher share of the raw material can be converted to recovered products. | |
| Higher energy consumption | | With the recovery of the solvent, the organosolv process consumes more energy than the dilute acid process. In Publication III, the energy consumption was found to be 34 % higher. The higher energy consumption and the higher total yield of recovered products resulted in the need of external fuel. |
| More complex flowsheet | | The recovery of solvent and by-products increases the number of processing steps (Publication III), which was in Publication IV found to result in a higher investment cost. |

As shown in the table above, the key technical advantage of the organosolv process is the ability to recover co-products. The most important co-product is the so-called organosolv lignin which is recovered by precipitation from the spent cooking liquor. The other co-products recovered in the process concept described in Publication III are furfural and acetic acid. Additional advantages of the organosolv process are related to the good enzymatic digestibility of the organosolv pulp and the possibility to produce a relatively pure C6 sugar stream from it. In the studied process concept these C6 sugars as well as the C5 sugars separated in the organosolv cooking were both directed to the same fermentation stage. For a downstream conversion requiring a C6 sugar stream with a low content of inhibitors, the organosolv concept would enable utilizing the C6 stream separately. Instead of breaking the pulp fraction to sugars, an additional opportunity would be to use the pulp in various cellulose applications, such as dissolving pulp. Taking into consideration the cost of enzymes and the considerable yield loss in the conversion of the pulp to ethanol, dissolving pulp could well be a more attractive end-use area for the organosolv pulp than ethanol.

The higher energy consumption and the larger number of processing steps are the major disadvantages of the organosolv process. The larger number of processing steps was in the economic analysis (Publication IV) found to result in a considerably higher investment cost. As discussed in Publication IV, there would be opportunities to decrease the investment cost of the organosolv process, by integrating to an existing industrial facility or by simplifying the process (e.g. by omitting the construction of the acetic acid recovery process). Also for example the optimization of water use could be a way to decrease both energy consumption and capital costs. One example of such optimization would be the precipitation of lignin through evaporation of ethanol instead of diluting with water, which would decrease the amount of water circulating in the system (see subchapter 4.5.2). The evaporation process would, however, need to be designed in a way to avoid fouling problems. The effect of the change in the precipitation method on the quality of the lignin product and its applicability in the intended end-use areas would furthermore need to be tested experimentally. In addition to the higher energy consumption and investment cost, also a potentially lower ethanol yield of the organosolv process was identified in Publication III as a disadvantage. The so-called carbohydrate-to-ethanol conversion rate was 64 % for the organosolv process and 76 % for the dilute acid process. While the difference can be potentially explained by the harsher conditions applied in organosolv cooking, it should, however, be noted that the mass balance data over the two pretreatment steps were derived from different sources (Pan et al. 2006; Humbird et al. 2011), with different experimental setups and raw materials. These factors can also explain to some degree the lower ethanol yield of the organosolv process that was assumed in the study.

The economic attractiveness of the organosolv process was assessed by calculating the so-called minimum ethanol selling price (MESP) for the produced ethanol and comparing it to the MESP of the dilute acid process. As discussed in Publication IV, the MESP of the organosolv process depended considerably on the assumed price of the organosolv lignin. The base case lignin price of 450 USD/t resulted in an MESP of 3.1 USD/gal (0.81 USD/L, 1030 USD/t), being higher than the MESP of the dilute acid process (2.6 USD/gal, 0.69 USD/L, 870 USD/t). Sensitivity analyses showed that a higher lignin price of 690 USD/t was required to bring the MESP of the organosolv process on a par with the MESP of the dilute acid process. Although improvements in e.g. energy consumption or capital intensity (such as those discussed above) could in principle lower the required sales price of lignin somewhat, the sensitivity analysis clearly demonstrated the crucial importance of identifying and developing higher-valued applications for the organosolv lignin.

As is highlighted in the discussion above, the organosolv process has advantages (particularly the recovery of co-products) and disadvantages (higher investment cost, poorer energy economy), and the price of lignin largely defines whether the advantages outweigh the disadvantages. A higher price of lignin is required for the organosolv process concept to be a competitive process for the production of second generation ethanol. The paying capability of organosolv lignin in different applications is ultimately defined by its functionality relative to competing products. One potential higher-valued application area for organosolv lignin is its use as a substitute for phenolic resins. In this application, organosolv lignin would need to compete both with the conventional, existing phenolic resin and with another lignin product, namely kraft lignin (see subsection 2.3.2). The price and performance would dictate which of these lignin types would be more competitive in this application area. Although organosolv lignin is a purer and more reactive type of lignin, kraft lignin has considerable advantages related to availability and maturity. There is already an existing supply of kraft lignin and a considerable future growth potential of the supply. Kraft lignin could therefore be a possible factor limiting the end-use opportunities of organosolv lignin and driving down its price potential.

As a general conclusion, it can be stated that the organosolv process could be attractive in ethanol production if higher-priced lignin applications could be developed. It should be kept in mind, however, that the economic analysis drew from a conceptual design that was based on data from laboratory-scale experiments. For a more detailed evaluation of the concept, data from pilot-scale experiments would be needed. As there is no commercial-scale production of organosolv lignin, it should be kept in mind that its value is very uncertain and there is no guarantee that a higher price could indeed be obtained for larger quantities of organosolv lignin. Also the time to market is an uncertainty. Commercializing a new type of type of material, in this case organosolv lignin, often requires a considerable amount of time. Data from application testing and market development work related to organosolv lignin would be needed to get a clearer picture of its price and market potential.

In this subchapter, also the potential use of organosolv process in the production of cellulose products, such as dissolving pulp, and the potential effect of emerging kraft lignin supply on the price and market potential of organosolv lignin briefly discussed briefly. These topics will be covered further in subchapter 6.6.

## 6.3 Theoretical contribution

This thesis presents the evaluation of two biorefinery concepts for the production of second generation ethanol. Both of the concepts have been evaluated in a comprehensive and systematic way. The theoretical contribution of the thesis relates both to the systematic approach utilized throughout the evaluation process and to the actual outcomes of the evaluations.

The extraction of hemicelluloses for the co-production of paper-grade pulp and co-products, such as ethanol, was widely studied in the academic world in the second half of the 2000s. The premise of this co-production concept was in more efficient utilization of hemicelluloses. Since a large share of hemicelluloses is dissolved in cooking and combusted in the recovery boiler, it was thought that water prehydrolysis before cooking would enable extracting them partially and converting them to more value-added products than energy. This was the premise also in the BiSe project (2007 – 2010) in which the thesis work related to hemicellulose extraction was carried out primarily in 2009 – 2010. Publications I and II, both published in 2010, contributed to the overall assessment of the viability of the concept. Publication I covered the integration of hemicellulose extraction and ethanol production process to a pulp mill and its effects on pulp mill operation. Publication II studied the effects of hemicellulose extraction on the quality of the pulp. These publications provided a systematic evaluation of the hemicellulose extraction, identifying several key disadvantages of the concept, including a considerable increase in wood consumption, increased load on the pulp mill recovery cycle, a small ethanol output, and a significant decrease in pulp beating response. These publications therefore contributed to the growing evidence that the studied concept had considerable drawbacks. In addition to the publications, a comprehensive literature review was presented in subchapter 3.1 of this thesis. The literature review both deepened the evaluation concerning the abovementioned aspects and extended it to the processability of the prehydrolyzate and to a review of published techno-economic assessments. This comprehensive review provided a solid basis for the evaluation of the overall viability of the concept. The systematic and thorough evaluation of the concept is one of the theoretical contribution of this thesis.

The evaluation of the organosolv concept was based on a conceptual process design and simulation model that covered the whole process from cooking to solvent and co-product recovery and ethanol production. The developed flowsheets and mass and energy balances were used as a basis for an economic assessment of the concept. The effects of co-products on the economics of the process were also studied. The organosolv process was compared technically and economically to the reference dilute acid pretreatment - based ethanol production concept (based on Humbird et al. 2011) as systematically as possible (see research question *Q3* in subchapter 5.6.2 for the methodology adopted in the comparison). Although a large number of studies on organosolv pulping had been published previously, no such comprehensive and systematic study on ethanol organosolv pulping for the production of ethanol were known to the author of this thesis. The comprehensive technical and economic assessment of the organosolv process concept and the systematic methodology adopted in its comparison to the dilute acid process are therefore theoretical contributions of the thesis.

## 6.4 Practical implications

The aim of this thesis was to evaluate the viability of two biorefinery concepts: hemicellulose extraction for the co-production of paper-grade pulp and ethanol, and organosolv pulping for the production of ethanol. The practical implications of the thesis relate directly to the findings of this evaluation. As discussed in subchapter 1.2, there are multiple different biorefinery concepts, and tools such as the Stage-Gate (see Figure 2) process can be used to manage product development and systemize project evaluation. Such tools and evaluations can then be used in managing a company's development project portfolio: to which projects resources should be allocated to and to which not. The evaluated process concepts were in this thesis considered to be particularly in the initial (concept) screening stage of the Stage-Gate procedure.

As is evident from the evaluation of the hemicellulose extraction concept (see subchapter 6.2.1), the concept was found to entail numerous disadvantages related to both the operation of the pulp mill and the conversion of the prehydrolyzate to ethanol. It was furthermore highlighted that as paper-grade pulp would be the main product, the viability of the concept would be largely dictated by the effect of water prehydrolysis on the quality of the produced pulp. Possible improvements in pulp quality could potentially offset the abovementioned disadvantages. As such improvements are in general not expected, the analysis carried out in this thesis therefore indicated that a process concept aiming for the co-production of a bulk-type paper-grade pulp and ethanol would not be attractive. In the Stage-Gate model, allocating further resources to the development of the kind of water prehydrolysis process studied and reviewed in this thesis would therefore not be recommendable. To justify the continuation of the development of this concept, the recovery and use of the prehydrolyzate would need to be studied in the context of dissolving pulp production. Alternatively a novel, specialty type of paper-grade pulp product benefiting from the specific properties of water prehydrolyzed pulp would need to be identified. A simple, yet considerably more selective extraction and cooking concept than the one studied in this thesis could possibly also merit continuation of the development work.

In the evaluation of the organosolv process (subchapter 6.2.2), the process was found to have both advantages and disadvantages compared to the reference dilute acid pretreatment -based ethanol production process. Higher energy consumption and capital costs were identified as particular disadvantages, and possible areas for improvement in these areas were discussed. The main advantage of the organosolv concept is the ability to recover co-products, particularly organosolv lignin. The price of lignin defines whether this advantage outweighs the disadvantages, thereby being a major factor contributing to the competitiveness of the concept. The economic analysis showed that a relatively high price was required for the organosolv process to be competitive with the reference process. As the conceptual process design was based on laboratory-scale experiments, and no application testing or market assessment for organosolv lignin were carried out, more detailed evaluation would, however, be required to improve the assessment of the concept.

Process development and experiments carried out in pilot scale could be used to validate and potentially improve the process design. As discussed in subchapter 6.2.2, one potential area for improvement in the process design is the use of water. More optimal use of water in the process would reduce both energy consumption and capital costs (with the very low concentration of the prehydrolyzate, water use was critical also in the hemicellulose extraction process, highlighting the overall importance of efficient water use in lignocellulosic biorefineries). The validated, and potentially improved, process design would in turn increase the accuracy of the cost estimations. With more accurate cost estimations, the minimum sales price of organosolv lignin required to make the process competitive with the reference dilute acid process could also be more accurately estimated. Simultaneous application testing and market development for organosolv lignin would give insight into whether such a sales price could be achieved or not. From the perspective of the Stage-Gate procedure, it would therefore be justifiable to allocate resources to a more detailed analysis of the concept.

As a summary of the practical implications, the findings of this thesis suggest that hemicellulose extraction through water prehydrolysis for the co-production of paper-grade pulp and ethanol would not pass the first gate review of the Stage-Gate procedure presented in Figure 2, unless a pulp application could be identified that would benefit from the properties of water-prehydrolyzed pulp, or the selectivity of the process could be improved considerably. The organosolv process, in turn, would pass to the next stage, where either pilot scale experiments or existing pilot scale data could be used to validate the process design and improve the accuracy of the cost estimations, while simultaneously carrying out application testing and market assessments to evaluate the potential applications, market sizes and pricing of organosolv lignin in closer detail.

## 6.5 Limitations of the research findings

The most suitable pretreatment and fractionation processes are always dependent on local, specific conditions. The type of raw material has its effects on the fractionation (see the discussion in subchapter 2.1.1). Also downstream processing has an effect. The choice of the pretreatment process could be different for a downstream process requiring a pure C6 sugar stream than for a more robust process being able to process a crude mixture of C5 and C6 sugars. Also company-specific factors, such as prior knowhow and assets, can have an effect on the selection of the fractionation technology. The overall pretreatment and fractionation field can furthermore be considered to be in an emerging stage, and new fractionation technologies are being developed. No universally optimal pretreatment technology can be expected to be found.

One example of local conditions is the effect of the assumed end-product on the evaluation of the two studied biorefinery concepts. The hemicellulose extraction process was evaluated from the perspective of co-producing paper-grade pulp and ethanol. The organosolv process concept also assumed the production of ethanol. Assuming other end-products could have changed the outcomes of the evaluation considerably. In the hemicellulose extraction concept, the most apparent one is producing dissolving pulp instead of paper-grade pulp. As discussed in subchapter 3.1.1, the prehydrolysis (hemicellulose extraction) step is conventionally used in the production of dissolving pulp. Unlike in the production of paper-grade pulp, where the aim is to retain hemicelluloses, prehydrolysis is required in dissolving pulp production because the hemicelluloses need to be removed selectively. In the production of dissolving pulp, the recovery of the prehydrolyzate and its conversion to ethanol or other products would therefore be free of most of the disadvantages of the hemicellulose extraction concept studied in this thesis (particularly increased wood consumption, increased load on the chemical recovery, impacts on pulp quality). The hemicellulose extraction concept can therefore be considered to be considerably more attractive in the production of dissolving pulp than in the production of general, bulk-type paper-grade pulp. Different assumptions concerning end-products could have also been made in the evaluation of the organosolv process concept (e.g. the production of dissolving pulp instead of ethanol), which would have required a different comparison point than the dilute acid process. The findings of the thesis are therefore limited to the specified end-products.

In addition to the limitations related to the scope of the study, one limitation concerns the choice of data and its uncertainty. The simulation models developed for the hemicellulose extraction and organosolv process concepts were largely based on laboratory-scale experimental data. It is generally uncertain how a scale-up to larger-scale equipment would affect the experimental data, and consequently the development of the simulation models and evaluations of the two process concepts. Some of the key parameters of the simulation models, for example the yields in the hemicellulose extraction stage (hemicellulose extraction process concept) and the yields in cooking (both of the studied process concepts), were furthermore based on selected, single experimental data points. The optimal process conditions can be different from those adopted in the simulation models. Both of these aspects can be sources of uncertainty in the thesis. Concerning the organosolv process, sensitivity analyses were run to capture the effect of a higher and lower sugar yield on the economics of the process. Larger-scale experimental work could be carried out to validate and improve the conceptual process design and the simulation model (see the following subchapter).

Concerning the hemicellulose extraction concept, the simulation model (Publication I) was based on laboratory experiments carried out in a very small scale (2 L reactors). The mass balance over water prehydrolysis and cooking was furthermore calculated on the basis of combined data from two separate sets of experiments (see subchapter 4.5.1). In other words, the experiments carried out in different locations with different reactors, temperature profiles in water prehydrolysis, and different sets of raw materials were assumed to result in compatible results. These are both potential sources of uncertainty. The mass balance over water prehydrolysis and cooking was, however, generally well in line with the literature (see Table 4), indicating that the mass balance in Publication I was justifiable and that the findings of Publication I can be generalized to cover also other raw materials than pine. The experiments carried out by Saukkonen et al. (2012b) in somewhat larger scale (30 L reactor) with the same type of raw material (pine) and similar conditions in water prehydrolysis (P-factor 200) also support the findings of Publication I, with the amount of organic material being 11.5 % (14.1 % in Publication I) and the yield on wood decreasing by 4.8 % percentage points (6.2 %). This indicates that the findings of Publication I are scalable, at least to some extent. Also the findings of Publication II concerning the quality of pulp are generally well in line with the literature: water prehydrolysis decreases the beating response and tensile strength and improves the tear strength.

## 6.6 Suggestions for further research

The suggestions for further research concern improving the accuracy of the evaluation of the studied organosolv concept, as well as evaluating other end-products and solvent systems. The current study provides a solid basis for studying these aspects.

As discussed in subchapter 6.2.2, experimental data from larger-scale experiments would be needed to validate and increase the level of accuracy of the process design and simulation model of the organosolv process. Simultaneously, the accuracy of the cost calculations would be increased, and improvements in the process design could be potentially carried out. Application testing and market development of the produced organosolv lignin would furthermore be required to get a more accurate estimate of its potential value. With the validated and potentially improved process design and the more accurate estimate of the value of organosolv lignin, a more reliable estimate of the competitiveness of the organosolv process concept could be made.

The organosolv process concept, fractionating lignocellulosic biomass to pulp, lignin and hemicellulosic sugar fractions, is a versatile platform that enables the production of various products. In addition to improving the accuracy of the current study, the evaluation of the organosolv process concept could therefore be expanded in future research beyond the production of ethanol. Which are the most attractive end-uses for the organosolv pulp fraction - fuels, chemicals or cellulosic applications? Which are the most attractive end uses for the hemicellulosic sugar stream?

As discussed in subchapter 6.2.2, one particular potential end-use area for the pulp fraction would be dissolving pulp. As with ethanol production, also in this application the viability of the organosolv process boils down to cost competitiveness. Is the organosolv process cost-competitive with state-of-the-art prehydrolysis kraft pulping process? As furthermore discussed in subchapter 6.2.2, kraft lignin, with existing supply and future supply growth potential, has considerable advantages against organosolv lignin. What are therefore the competitive advantages of organosolv pulping over kraft pulping? Further research could evaluate the competitiveness of the organosolv process against kraft pulping.

In addition to different products and comparison against kraft pulping, also other process concept than ethanol-based cooking could be studied. Which are the most attractive solvent systems and process designs for an organosolv biorefinery?

# 7 Conclusions

The viability of two biorefinery concepts, namely hemicellulose extraction for the co-production of paper-grade pulp and ethanol, and organosolv pulping for the production of ethanol were evaluated in this study. Hemicellulose extraction by prehydrolysis is conventionally applied in the production of dissolving pulp. The concept has been studied also in combination with paper-grade pulp production. This topic was particularly popular in the academic world in the second half of the 2000s. The premise of this paper-grade pulp production concept was in more efficient utilization of hemicelluloses: a large share of hemicelluloses is dissolved in cooking and combusted in the recovery boiler. Water prehydrolysis before cooking would enable extracting them partially and converting them to more value-added products than energy. This was the premise also in the BiSe project (2007 – 2010) in which the thesis work related to hemicellulose extraction was carried out primarily in 2009 – 2010.

It was, however, found both in Publications I and II (in which softwood was used as raw material) and in the literature reviewed in this thesis that the extraction of hemicelluloses through water prehydrolysis has considerable drawbacks. The extraction results in considerable loss of the overall yield on wood. At constant pulp production, this increases the wood consumption considerably. The digester yield has furthermore been found to decrease in most published studies. In other words, the extraction of hemicelluloses results in an increased, not decreased, amount of organic material dissolved in cooking. Water prehydrolysis cannot therefore be considered to lead to more efficient utilization of hemicelluloses. In addition to increased wood consumption, other major disadvantages are an increased load on the evaporation plant and recovery boiler, as well as difficult processing of the produced prehydrolyzate and a small scale of ethanol production. In addition, the effects of water prehydrolysis on the quality of the produced pulp are inconclusive at best. The concept cannot therefore be considered attractive for general paper-grade pulp production. This is by no means a surprising conclusion. The general trend in the industry is to maximize the pulp yield, not to decrease it with unnecessary process steps. While being outside the scope of this thesis (co-production of paper-grade pulp and ethanol), it should be kept in mind that prehydrolysis in combination with kraft pulping is common practice in dissolving pulp production. The recovery and use of the sugars present in the prehydrolyzates of dissolving pulp production would be considerably more attractive than the concept studied in this thesis.

Organosolv pulping was originally designed for the production of paper-grade pulp. As the produced pulp has a good response to enzymatic hydrolysis, it has also been considered as a potential pretreatment and fractionation step in the production of lignocellulosic ethanol or other biofuels or chemicals. As mentioned above, in this thesis organosolv cooking was studied from the perspective of ethanol production. The research work was carried out primarily between summer 2010 and autumn 2011. The work resulted in Publications III and IV, published in 2013 and 2014.

As a pretreatment and fractionation step for bioethanol production, the key advantage of organosolv pulping is the ability to recover so-called organosolv lignin, which is a lignin product with high purity and narrow molecular weight distribution. The solvent used in cooking needs, however, to be recycled efficiently, which adds to the complexity of the process, increasing capital costs and energy consumption. The price of organosolv lignin largely dictates whether the advantage related to its recovery outweighs these two disadvantages. The economic assessment carried out in this thesis indicated that a lignin price considerably higher than its energy value would be needed to make the process competitive with the reference dilute acid pretreatment -based ethanol production process. This demonstrated the importance of finding higher-valued applications for the lignin.

The conceptual process design of the organosolv process was based on laboratory-scale experiments, and no application testing or market assessments were carried out for organosolv lignin. As a general conclusion, it can therefore be stated that the organosolv concept can be generally considered attractive if higher-priced applications for organosolv lignin can be identified. Data from pilot-scale experiments, as well as application testing and market development work related to organosolv lignin would be needed to improve the accuracy of the evaluation of the concept.

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# Publication I

Kautto, J., Henricson, K., Sixta, H., Trogen, M. and Alén, R.
**Effects of integrating a bioethanol production process to a kraft pulp mill**

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# Publication II

Kautto, J., Saukkonen, E. and Henricson, K.
**Digestibility and paper-making properties of prehydrolyzed softwood chips**

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# DIGESTIBILITY AND PAPER-MAKING PROPERTIES OF PREHYDROLYZED SOFTWOOD CHIPS

Jesse Kautto,[a*] Esa Saukkonen,[b] and Kaj Henricson [b]

The effect of hemicellulose extraction of pine wood chips by water prehydrolysis on subsequent kraft cooking and paper properties was studied. Prehydrolysis reduced the required cooking time by approximately 40% and increased kappa number reduction in oxygen delignification. Prehydrolysis decreased the overall brownstock pulp yield on wood by 7.2 percentage units. Consequently, valuable products would need to be produced from the prehydrolyzate to compensate for the resulting increase in wood consumption. In DED-bleaching, lower bleaching chemical dosages were needed with prehydrolyzed than with unhydrolyzed pulps to obtain similar final brightness. As expected, removal of hemicelluloses led to a decrease in the tensile index and increase in the tear index. At a given density, the strength potential of prehydrolyzed pulps was higher than that of unhydrolyzed pulps. There was an up to more than fivefold increase in beating revolutions in a PFI-mill needed to obtain comparable tensile indices. This significant reduction in beating response might pose problems in the commercialization of prehydrolyzed pulps. In general, differences between the paper properties of prehydrolyzed pulps and unhydrolyzed pulps are attributed to decreased inter-fiber bonding in prehydrolyzed pulps.

*Keywords: Water prehydrolysis; Cooking; Bleaching; Beating; Paper-making properties*

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## INTRODUCTION

The finite nature of fossil fuels and their contribution to carbon dioxide emissions have motivated increasing interest in biofuels. This, in turn, has led to the development of various biorefinery concepts (see, e.g. Kamm and Kamm 2004) in which biomass is converted to biomaterials and biofuels in fully integrated systems. Existing forest industry facilities could play a key role in the utilization of lignocellulosic biomass, as the people who run such facilities already possess the know-how, logistics, and infrastructure for procuring, transporting and processing lignocellulosics. Thus, different biorefinery concepts aimed at combining biofuel production with pulp and paper production have attracted interest in academia and industry. These concepts can be called, e.g., integrated forest biorefineries (IFBR) (van Heiningen 2006).

One option to convert a pulp mill into a pulp and biofuels and/or biochemicals producing biorefinery would involve the extraction of hemicelluloses from wood chips. As a steam-phase prehydrolysis process, hemicellulose extraction is conventionally used in the production of high-purity dissolving pulps. Carried out in an aqueous phase, hemicellulose extraction could enable the extraction of valuable hemicelluloses prior to kraft paper pulp production. Hydrolyzation of hemicelluloses to monomeric sugars with fermentation to ethanol would enable the co-production of ethanol and pulp. An existing pulp mill in Old Town, Maine, USA, is currently being converted to a biorefinery utilizing hemicellulose extraction technology (Pendse *et al.* 2009). In addition to ethanol, other products and chemicals could also be produced from hemicelluloses, such as films and coatings (Hansen and Plackett 2008). The sugars formed in the hydrolysis of hemicelluloses could be used to produce various chemicals; a U.S. DOE study lists over 300 potential building block chemicals that could be produced from sugars and synthesis gas of biomass (Werpy et al. 2004).

The extraction of hemicelluloses from wood chips can be done prior to cooking in a so-called pre-extraction process. Several methods for the extraction of hemicelluloses have been reported. In a prehydrolysis process, the hemicelluloses are hydrolyzed to oligomeric and monomeric sugars with the aid of, for example, pressurized hot water (autohydrolysis) (e.g. Casebier et al. 1969; Garrote and Parajo 2002; Yoon et al. 2008; Al-Dajani et al. 2009; Leschinsky et al. 2009), dilute acids (e.g. Parajó et al. 1994; Frederick. et al 2008; Al-Dajani et al. 2009) or steam (e.g. San Martín et al. 1995). Hemicelluloses can also be extracted by alkaline extraction before (e.g. van Heiningen et al. 2008; Al-Dajani and Tschirner 2008) or even after pulping (Pekkala 2008).

When commercializing these hemicellulose pre-extraction processes, their effect on the kraft fiber line and on the papermaking properties of subsequent pulps is of key importance. The extraction of hemicelluloses has been reported to affect cooking (Sixta 2006a; Smith et al. 2008; Yoon and van Heiningen 2008; Al-Dajani et al. 2009), $O_2$-delignification (Antonsson et al. 2003; Sixta 2006b,c), hornification and swelling tendency (Oksanen et al. 1997; Moss and Pere 2006), beating response (Vaaler et al. 2002; Yoon and van Heiningen 2008), and strength properties (Spiegelberg 1966; Rydholm 1967; Kettunen et al. 1982; Molin and Teder 2002). Although several studies on the effect of hemicellulose extraction on various isolated aspects of fiber line and paper-making properties have been published, more comprehensive studies on the pulping and paper making properties of hemicellulose-extracted chips are lacking. Yoon and van Heiningen (2008) have studied the digestibility, beatability, and paper properties of hot-water prehydrolyzed loblolly pine (*Pinus Taeda*) chips. With the exception of Yoon and van Heingingen (2008), there appear to be no studies comprising the whole fiber line, including bleaching and testing of bleached sheets. There is therefore a need for a study examining the whole fiber line, from hemicelluloses extraction and cooking to testing of bleached pulps.

This paper is part of the *Biojalostamo Sellutehdas (BiSe)* project, studying the conversion of a conventional kraft pulp mill into a pulp and biofuel-producing biorefinery. It is continuation to a paper presented elsewhere (Kautto et al. 2010) in which the integration of a prehydrolysis bioethanol process to a kraft pulp mill was discussed. This paper discusses the effect of water prehydrolysis of pine wood chips on cooking, oxygen delignification, bleaching, beating, and paper properties.

## EXPERIMENTAL

The cooking experiments were carried out in the Department of Forest Products Technology at Aalto University, School of Science and Technology. The pulp beating, bleaching, and papermaking property experiments were carried out at

NabLabs Oy, Rauma, Finland.

## Materials

The wood raw material used was industrial pulp wood chips collected from a pulp mill located in South-East Finland. The raw material was mainly Scots pine (*Pinus Sylvestris*), and the sample possibly contained some amount of Norway spruce (*Picea Abies*). The industrial wood chips were screened (SCAN-CM 40:01). The accepts were the fraction passing 7 and 13 mm slot sizes. The fraction was then manually checked for knots and bark.

## Methods

The experiments were carried out for an unhydrolyzed reference pulp (**pulp 1**) and for prehydrolyzed pulps cooked at sulfidity levels of 40% (**pulp 2**) and 20% (**pulp 3**). The reference pulp 1 was cooked at a sulfidity level of 40% and then bleached. Pulps 2 and 3 were first prehydrolyzed with hot water at 150 °C and then cooked and bleached.

### *Prehydrolysis at P-factor 200*

Pulps 2 and 3 were prehydrolyzed with hot water for the extraction of hemicelluloses. In the prehydrolysis, 3000 g of pine wood chips were placed in a 20 liter digester. Deionized hydrolysis water was then introduced to the digester to obtain a liquor-to-wood ratio of 4.6 L/kg. The mixture was first heated to 80 °C, and then to 150 °C at a rate of 2 °C/min. The mixture was kept at 150 °C for 1 h 33 min. This corresponds to a P-factor of 200. The P-factor is a term representing the severity of a hot water hydrolysis treatment. The P-factor was calculated from the recorded temperature/time data according to Sixta (2006a), based on an activation energy of 125.6 kJ/mol. After the set time, a valve was opened at the bottom of the digester, and the hydrolysis liquor (prehydrolyzate) was drained from the digester. The wood chips were then cooked. There was no intermittent chip washing between prehydrolysis and cooking.

### *Cooking*

The cooking was carried out in the same digester as used in the prehydrolysis. With pulps 2 and 3, the hydrolyzate was drained from the digester after prehydrolysis. With pulp 1, 3000 g of chips were placed in the digester. 1 liter of deionized water was introduced to the digester. The liquid-to-wood ratio was then adjusted to 4.6 by adding deionized water and cooking chemicals. The effective alkali (EA) level during cooking was 20%, expressed as NaOH based on oven dry wood, in all cooks. The sulfidity level was 40% for pulps 1 and 2 and 20% for pulp 3. The digester was first heated to 80 °C, and then to the cooking temperature of 160 °C at a rate of 1.5 °C/min. The cooking was stopped at an H-factor of 1600 in the case of the reference pulp. This H factor corresponded to a cooking time of 3 h 51 min. With pulp 2, the cooking was stopped at an H-factor of 1000 (cooking time of 2 h 22 min), and with pulp 3, the cooking was stopped at an H-factor of 1300 (3 h 6 min). Draining of the digester was started two minutes before the set cooking time. After the set cooking time had been reached and the digester had been drained, the digester was filled with NaOH solution (5 g/L). The mixture was then heated to 80 °C and kept at 80 °C for 10 minutes. It was subsequently drained, and the digester was filled with deionized water. The mixture was similarly heated to 80 °C and kept at 80 °C for 10 minutes.

After that, the water was drained and the NaOH solution treatment was repeated two times. The pulp was then removed from the digester, centrifuged, homogenized, and weighed. Its dry solids content was measured according to SCAN-C 3:78. The metal content of the pulps was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

### *Screening*

The pulps were first wet disintegrated and then screened with a TAP031 screener with a 0.25 mm slot size. The accepts fraction was then homogenized. The dry solids content of the accepts and rejects was then analyzed according to SCAN-C 3:78.

### *Bleaching*

All pulps were oxygen delignified and subsequently bleached with a DED-sequence. Oxygen delignification was done for 600 gram pulp batches in a 16 litre rotating pressurized cooking apparatus. The count for the 30-minute reaction time started when the temperature of the cooking apparatus reached 89 °C. After oxygen delignification the pulps were washed three times with 12 litres of deionized water and homogenized for three minutes with a Tripas Planet kitchen mixer.

Unpressurized laboratory bleaching was carried for 300 gram pulp batches in plastic bags in a hot water bath. $ClO_2$ for the bleaching stage was acquired from a pulp mill located in Western Finland as a water solution. Appropriate safety measures were taken in handling the solution and the D bleaching stage (ventilated hood, safety goggles and mask etc.). Chemical charges used in the bleaching stages $D_0$ and E were calculated from the kappa number after $O_2$-delignification. Chemical charge in the $D_1$-stage was the same for every pulp batch. Pulps were washed two times with 60 litres of deionized water after the $D_0$- and $D_1$-stages and a similar procedure plus an additional wash with 20 litres of deionized water was applied after the E-stage. The oxygen delignification and bleaching conditions for all pulps are presented in Table 1.

**Table 1.** Oxygen Delignification and Bleaching Conditions with Chemical Charge Amounts

| Sequence | **O** | **$D_0$** | **E** | **$D_1$** |
|---|---|---|---|---|
| Pulp consistency, % | 10 | 10 | 10 | 10 |
| Act. Cl charge % | | 0.2×incoming kappa | | 1 |
| NaOH charge % | 2 | | 0.6×$D_0$ charge | |
| Temperature, °C | 90 | 60 | 60 | 70 |
| Time, min | 30 | 45 | 75 | 180 |
| Pressure, bar | 5 | | | |
| Target end pH | | ~2 | ~12 | ~3.6 |

Viscosity (ISO 5351-1:1981) of the pulp samples was measured after $O_2$-delignification and bleaching stages E and $D_1$. The ISO brightness (ISO 2470:1999) of the pulp samples was measured after $O_2$-delignification and bleaching stages E and $D_1$. Kappa numbers (ISO 302:2004) were determined before and after oxygen delignification.

### *Handsheet properties*

The mechanical properties of the pulps were evaluated by handsheet testing (ISO 5270:1998). The pulps were refined in a PFI mill (ISO 5264-2:2002), handsheets were prepared (ISO 5269-1:1998) with different degrees of beating, and the CSF-values were measured (ISO 5267-2:2001).

## RESULTS AND DISCUSSION

### The Effect of Prehydrolysis on Cooking and Oxygen Delignification of Chips

Prehydrolysis of the wood chips was carried out at P-factor of 200 at 150 °C. For prehydrolyzed pulps 2 and 3 the hydrolyzate was then drained from the digester and the chips were cooked and oxygen delignified. With constant conditions in oxygen delignification, the target kappa number after $O_2$-delignification was 15 for all pulps. Based on earlier experiments on smaller scale laboratory digesters (presented in Kautto et al. 2010), it was assumed that prehydrolyzed chips can be cooked at lower H-factors and that they respond better to $O_2$-delignification. The cooking of prehydrolyzed chips was therefore carried out with lower H-factors, and the target kappa numbers after cooking were higher. Pulp 2 was cooked at an H-factor of 1000 at a sulfidity level of 40% and pulp 3 at an H-factor of 1300 at a sulfidity level of 20%. The reference chips (pulp 1) were cooked at an H-factor of 1600. Figure 1 presents the yields on wood and kappa numbers of prehydrolyzed and unhydrolyzed chips after cooking and $O_2$-delignification. Table 2 presents the yields on wood, kappa numbers, residual alkalis, viscosities, and ISO-brightnesses after cooking and $O_2$-delignification.

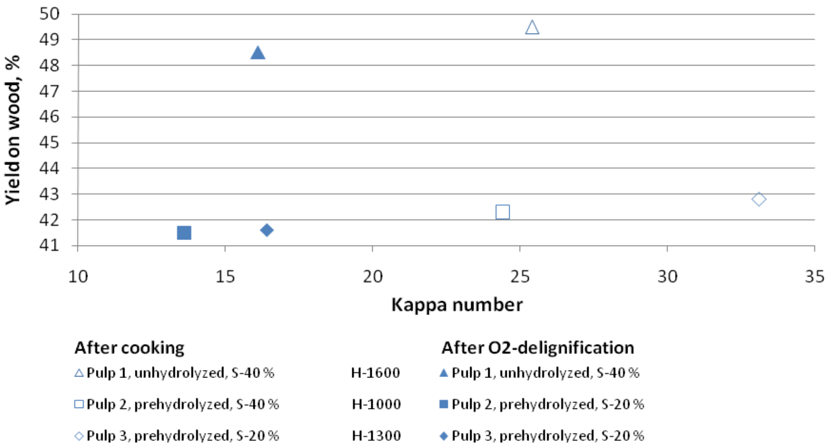

**Fig. 1.** Yield on wood versus kappa number after cooking and oxygen delignification of pulp 1 (unhydrolyzed reference chips cooked at a sulfidity of 40% at an H-factor of 1600) and pulps 2 and 3 (chips prehydrolyzed at a P-factor of 200 and cooked at an H-factor of 1000 and a sulfidity level of 40%, and at an H-factor of 1300 and a sulfidity level of 20%, respectively). Effective alkali level was 20% in all cooks.

**Table 2.** Yield on Wood, Kappa, Residual Alkali, and Viscosity after Cooking for Pulps 1, 2, and 3

| | Cooking | | | | $O_2$-delignification | | | |
|---|---|---|---|---|---|---|---|---|
| Pulp | Yield on wood, % | Kappa | Residual alkali, g/l | Viscosity, ml/g | Yield on wood, % | Kappa | ISO-brightness | Viscosity, ml/g |
| 1 | 49.5 | 25.4 | 7.9 | 1280 | 48.5 | 16.1 | 37.7 | 1055 |
| 2 | 42.3 | 24.4 | 9.8 | 1320 | 41.5 | 13.6 | 42.5 | 1070 |
| 3 | 42.8 | 33.1 | 10.5 | 1280 | 41.6 | 16.4 | 39.4 | 1010 |

As can be seen in Fig. 1, at similar sulfidity levels of 40%, the H-factor can be lower with prehydrolyzed chips to obtain similar kappa numbers. The H-factors for reference and prehydrolyzed chips were 1600 and 1000, and kappa numbers after cooking were 25.4 and 24.4, respectively. With a cooking temperature of 160 °C and a heating rate of 1.5 °C/min, this would be equivalent to a shortening of the cooking time from 3 h 51 min to 2 h 22 min (39%). This is in line with the findings of Yoon and van Heiningen (2008), who report that with approximately 5% to 8% of wood material (loblolly pine) extracted during water prehydrolysis, the delignification rate constants in the subsequent kraft cooking are 40% to 60% higher than with unhydrolyzed chips. The lower required H-factors and higher delignification rates would imply that the digestibility of prehydrolyzed chips is higher. The enhanced delignification of prehydrolyzed chips has been attributed to improved permeability of the cell wall caused by increased pore volume, resulting in improved penetration of the cooking liquor, and hydrolytic cleavage of lignin structures and covalent bonds of lignin-carbohydrate complexes (LCC) during pre-extraction (Sixta 2006a). The shortened cooking time could potentially enable a capacity increase in cooking. Reducing the sulfidity level from 40% to 20% in cooking of prehydrolyzed chips (pulps 2 and 3) increases the required H-factor. As expected, the higher sulfidity level would therefore seem to increase the delignification rate in the cooking of prehydrolyzed chips.

As can be seen in Table 2, the yields on wood after cooking of pulps 1 and 2 are 49.5% and 42.3%, respectively. To obtain a similar brownstock pulp production, this 7.2 % percentage unit drop in yield on wood would signify an increase in wood consumption by approximately 17%. This is in agreement with our previous results (Kautto et al. 2010), where a 16% wood consumption increase was calculated based on smaller-scale prehydrolysis and cooking experiments. This would imply that potentially more valuable products than biofuels would need to be produced from at least part of the prehydrolyzate to compensate for the rather significant increase in wood consumption. The determination of the minimal values of the products produced from the prehydrolyzate requires careful economic analysis of the prehydrolysis process. A comprehensive economic analysis of the process is, however, beyond the scope of this study.

The composition of the hydrolyzate was not analyzed in this set of experiments. A thorough mass balance calculation of the prehydrolysis and cooking could not therefore be carried out. However, assuming that 14.1% of wood material (approximately 50% of which being carbohydrates) would be dissolved at P-factor 200 at a temperature of 150 °C as in our previous experiments (Kautto et al. 2010, note a smaller-scale digester, different temperature profile of prehydrolysis and a different set of raw material), the cooking yield of pulp 2 would be 49.2%. Taking into consideration that the kappa number after cooking was slightly lower with pulp 2, it would seem that the cooking yields of water prehydrolyzed and unhydrolyzed softwood pulps are rather similar. In the literature, prehydrolysis has however been reported to decrease the cooking yield. With 5.0% and 7.0% of loblolly pine pre-extracted in water prehydrolysis at 170 °C, Yoon and van Heiningen (2008) present the yields on wood after cooking to be approximately 42.5% and 39.5%. Based on these extraction amounts and pulp yields, and a yield of approximately 45.5 % of unhydrolyzed pulps at equal kappa numbers, the cooking yields can be calculated to be approximately 0.8 and 2.6 percentage units lower with prehydrolyzed chips. Similarly, cooking yield decreases of approximately 3 to 4% units can be calculated based on the results of Al-Dajani et al. (2009) where 19% of aspen wood was dissolved in water prehydrolysis at 150 °C for 4.5 h prior to cooking. It would therefore seem that pre-extraction of hemicelluloses prior to pulping either leads to degradation of carbohydrates that would be stable in conventional kraft pulping with no pre-extraction in the prehydrolysis stage, or it enhances such degradation in the cooking stage, thus lowering the cooking yield. Based on earlier experiments with a different reactor and a different batch of raw material, a slightly too high assumption of 14.1% of wood extracted in prehydrolysis could possibly explain the seemingly similar cooking yields of unhydrolyzed and prehydrolyzed chips found in this study.

Under constant conditions of oxygen delignification, kappa reduction was significantly higher with prehydrolyzed chips than with reference chips. The kappa number was reduced by approximately 37%, 44%, and 50% with pulps 1, 2, and 3, respectively. This improved response to $O_2$-delignification allows stopping of the cooking at higher kappa numbers with prehydrolyzed chips. The better response of prehydrolyzed chips to oxygen delignification has previously been shown for E. saligna hardwood chips (Sixta 2006b). The increased kappa reduction of hemicellulose-poor prehydrolyzed chips is also in line with the findings of Zou et al. (2002). By varying the xylan content of brownstock hardwood kraft pulp with the use of anthraquinone, they found that a higher amount of xylan decreases the rate of oxygen delignification. This would imply that the amount of xylan affects the accessibility of the chemical reactants in the $O_2$-stage. The higher kappa reduction of prehydrolyzed pulp 3 than that of prehydrolyzed pulp 2 could probably be explained by the higher kappa number before $O_2$-stage. It has been shown that a higher kappa number after softwood kraft cooking leads to a higher kappa number reduction in subsequent $O_2$-delignification (Poukka et al. 1999). Possibly, this is because pulps with higher kappa numbers after cooking contain a larger amount of easily removable lignin fragments. With low residual kappa numbers, pulps have been shown to contain relatively more LCCs that are difficult to delignify (Lawoko et al. 2004).

In addition to kappa number reduction, the response of pulps to $O_2$-delignification can also be characterized by selectivity. Selectivity is normally defined as the reduction of viscosity per kappa unit. Based on data presented in Table 2, the selectivities of pulps 1, 2, and 3 would be approximately 24.2, 23.1, and 16.2 $(\Delta \text{ml/g})/\Delta \text{kappa}$, respectively. The selectivity of prehydrolyzed S-40% pulp would therefore seem to be slightly better, and the selectivity of prehydrolyzed S-20% pulp significantly better than that of the reference pulp. Interestingly, selectivity has been reported in the literature to be enhanced with increasing hemicellulose content (Zou et al. 2002; Zou 2002). One explanation for this finding has been that hemicelluloses act to protect the cellulose from radical attack of free hydroxyl radicals (OH·) (van

Heiningen and Violette 2001; Zou et al. 2002), thus hindering cellulose degradation. The peeling reactions of hemicelluloses would also consume alkali, thus decreasing the amount of alkali available to react with cellulose. The amount of cellulose and its degree of polymerization are the major contributors to the viscosity of pulp due to its high degree of polymerization (Zou et al. 2002). Unlike in the experiments of Zou et al. (2002), where initial kappa numbers were low (16.3 to 17.6) and the kappa number reductions in the $O_2$-stage were rather low and uniform (approximately 35% to 38%), the kappa numbers in this work and consequently also the kappa number reductions were higher. The kappa number reductions also varied more significantly, being higher with prehydrolyzed chips. Although the viscosity loss of pulp 1 (225 ml/g) was lower in the $O_2$-stage than that of pulps 2 and 3 (250 and 270 ml/g), the selectivities of prehydrolyzed chips were higher. In this work, it would therefore seem that the higher kappa number reductions of prehydrolyzed chips contributed more to the selectivity than the loss of viscosity.

## The Effect of Prehydrolysis on Bleachability of Pulps

The term bleachability is used to describe the ease of bleaching of a given pulp, but there is no standard method to evaluate the bleachability of pulps. Usually, bleachability of pulp is the consumption of bleaching chemicals required to reach a given brightness. Results from bleaching of pulps 1, 2, and 3 are presented in Table 3. The chemical consumptions as total active chlorine (kg Cl/ton of pulp) in the DED-bleaching sequence are shown in Fig. 2.

**Table 3.** Bleaching Chemical Dosages in the DED-sequence and the Development of ISO-brightness and Pulp Viscosity in Bleaching

| Pulp | Kappa after $O_2$-stage | Stage | Act. Cl, kg/tp | NaOH, kg/tp | End pH | Brightness, ISO % | Viscosity, ml/g |
|---|---|---|---|---|---|---|---|
| 1 | 16.1 | $O_2$ | | 20 | | 37.7 | 1055 |
| | | $D_0$ | 32.2 | | 1.9 | | |
| | | E | | 19.3 | 12.6 | 54.7 | 1037 |
| | | $D_1$ | 10 | | 3.6 | 74.1 | 998 |
| 2 | 13.6 | $O_2$ | | 20 | | 42.5 | 1070 |
| | | $D_0$ | 27.2 | | 1.7 | | |
| | | E | | 16.3 | 12.5 | 58.1 | 1018 |
| | | $D_1$ | 10 | | 3.8 | 73.7 | 990 |
| 3 | 16.4 | $O_2$ | | 20 | | 39.4 | 1010 |
| | | $D_0$ | 32.8 | | 1.7 | | |
| | | E | | 19.7 | 12.6 | 56.2 | 953 |
| | | $D_1$ | 10 | | 3.7 | 71.9 | 935 |

As can be seen in Table 3, pulp 2 had higher brightness and a lower kappa number than pulp 1 after the oxygen delignification stage. Yet, prehydrolyzed pulp 2 did not reach a higher final brightness than unhydrolyzed pulp 1 after DED-bleaching, final brightnesses being 73.7% and 74.1%, respectively. However, the lower kappa number after $O_2$-delignification of prehydrolyzed pulp 2 enabled a lower $ClO_2$-charge in the $D_0$-stage (15.5% lower, calculated as total active chlorine). This resulted in lower total chemical consumption in the DED-bleaching sequence, with no losses in viscosity, when the target was to reach a final ISO-brightness of 74%. At the same time, pulps 1 and 2 showed no remarkable difference in bleachability calculated as (OXE/ton)/Δkappa in the DED-sequence. Cooking of prehydrolyzed chips with a lower sulfidity level of 20% resulted in a lower final brightness (71.9%) even with the highest chemical charge calculated as total active chlorine.

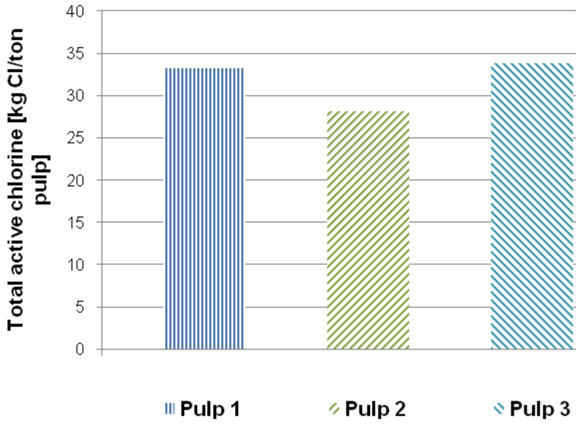

**Fig. 2.** Total chemical consumption in the DED-sequence calculated as total active chlorine (kg Cl/ton of pulp). Final brightnesses for pulps 1, 2, and 3 were 74.1%, 73.7%, and 71.9%, respectively.

A higher level of hydrosulfide ions in cooking, i.e. higher sulfidity, is known to have a slightly positive effect on unbleached brightness (Axelsson 2004, Gustavsson et al. 1999) and leads to better brightness development during ECF bleaching (Neto et al. 2002; Axelsson 2004). Based on our data, it can be said that the correlation between sulfidity level in cooking and pulp bleachability is markedly the same, whether or not the chips are prehydrolyzed prior to cooking. Figure 3 depicts the brightness gain throughout (O)DED-bleaching and chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp) of unhydrolyzed pulp 1 and prehydrolyzed pulps 2 and 3.

As can be seen in Fig. 3, prehydrolyzed pulp 2 reached the same final brightness in (O)DED-bleaching as unhydrolyzed pulp 1 with lower chemical dosage calculated as total active chlorine (kg C/ton of pulp). Lowering the sulfidity level for prehydrolyzed pulp in cooking from 40% to 20% caused increases in chemical consumption and hindered the attainment of equally high final brightness. The same trend of increased chemical consumption and difficulties in reaching equally high brightness levels as with pulps 1 and 2 was even more pronounced with non-sulfur cooking of prehydrolyzed chips (data not shown).

Since prehydrolysis affects various aspects in the cooking process and pulp composition, some potential indirect effects of prehydrolysis on pulp bleaching will be discussed in the following paragraphs. To analyze the significance of these factors individually requires, however, further studies.

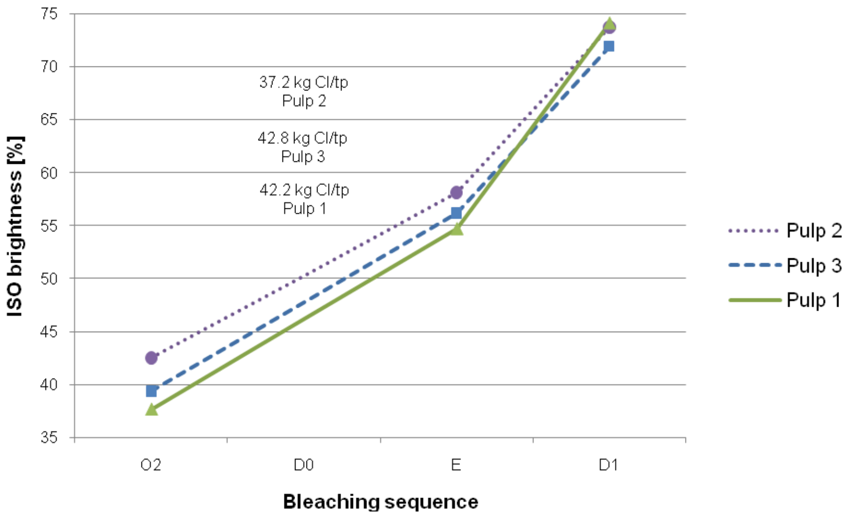

**Fig. 3.** ISO-brightness development in (O)DED-bleaching for prehydrolyzed pulps with chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp).

### *Effect of cooking H-Factor on bleachability*

Low H-factor is known to be beneficial for the bleaching response of pulp, at least for *Eucalyptus globulus* kraft pulps (Neto et al. 2002). A lower H-factor in cooking also results in a higher amount of alkyl-aryl ether linkages (β-O-4 structures) in residual lignin, and these kinds of pulps exhibit low specific absorption coefficients, i.e. better bleachability (Gustavsson et al. 1999). In the experiments described in this paper the prehydrolyzed pulp 2 was cooked with a lower H-factor than the unhydrolyzed pulp 1; H-factors being 1000 for prehydrolyzed and 1600 for unhydrolyzed pulp. The considerably lower H-factor of prehydrolyzed pulp 2 did not, however, lead to an increase in bleaching response compared with the reference pulp 1. One possible explanation is that the lignin fraction in water prehydrolyzed pulp has already experienced undesirable acid condensation reactions and loss of β-O-4-linkages in the prehydrolysis step, overruling the effect of a lower H-factor in cooking. Structural and chemical changes of lignin and breakage of ether linkages in water prehydrolysis have been suggested also by other authors (Antal 1996; Mosier et al. 2005; Leschinsky et al. 2007; 2008) , but the lack of effective analytical methods for evaluating lignin, both its structure and its chemical composition, hinders more complete understanding of this phenomenon (Mosier et al. 2005).

### *Effect of hexenuronic acids on bleachability*

During kraft pulping, 4-*O*-methylglucuronic acid groups attached to xylan are partially converted to hexenuronic acid groups, forming hexenuronoxylan (Jiang et al. 2000). Hexenuronic acids (HexA) contribute to the measured kappa number in kraft pulps, 3-6 kappa number units for hardwood kraft pulp and 1-3 kappa number units for softwood kraft pulps (Gellerstedt and Li 1996). Based on previous studies (Antonsson et al. 2003; Liu et al. 2009), it is likely that the generation of hexenuronic acids during cooking is lower with prehydrolyzed pulp, since a proportion of softwood xylan is removed from the wood chips in the prehydrolysis step. Consequently, the amount of 4-O-methylglucuronic acid (MeGlcA) sidegroups attached to xylan are diminished in the pulp by respective ratio, thus lowering the amount of MeGlcA sidegroups converted to HexA during cooking of prehydrolyzed chips.

Hexenuronic acids are known to play an important role in consuming electrophilic bleaching agents such as ozone and chlorine dioxide (Vuorinen et al. 1996) and have been found to be as reactive as lignin towards these electrophilic bleaching chemicals (Vuorinen et al. 1997). In addition to increased consumption of bleaching chemicals, hexenuronic acid groups cause greater brightness reversion and poorer metal removal (Jiang et al. 2000). Therefore, when comparing water prehydrolyzed and unhydrolyzed softwood pulp, the difference in the HexA amount of unbleached pulp might also have an effect on chemical consumption in bleaching. The hexenuronic acid content of the unbleached pulps was not determined in this work, and the significance of this assumption to bleaching results should thus be verified with further studies.

### *Effect of metal content of pulp*

Dahl et al. (1998) have studied the role of transition metal content in the D stages of pulp bleaching. According to these authors, manganese and especially iron in the process water cause loss of brightness; iron also has a detrimental effect on pulp viscosity. Lachenal et al. (1998) reported that iron in chlorine dioxide bleaching may generate Cl· radicals and therefore cause depolymerisation of carbohydrates, reducing the viscosity of pulp.

According to Sjöström (1993), transition metals in wood and pulp suspensions are partially bound to the carboxyl groups present in xylan and pectins held by the forces complexing the wood constituents, or existing as free ions in the water. Transition metals can easily be displaced and washed out of a pulp suspension (Dahl 1999). Heavy metals such as Fe and Mn can be assumed to be partially washed away somewhat similarly from wood chips in the acidic conditions of water prehydrolysis, since such metal ions can be displaced and washed out from wood by aqueous acids (Sjöström 1993).

In our study the content of the transition metals manganese and copper was lower for prehydrolyzed than for unhydrolyzed pulp, but the amount of iron in prehydrolyzed pulps was markedly higher than for unhydrolyzed pulp (see Table 4 below). High amounts of iron may have hindered the bleachability of the prehydrolyzed pulps. Since the content of other transition metals (Mn, Cu) in prehydrolyzed pulps decreased, it can be concluded that the excess iron was probably derived from the interior wall of the prehydrolysis/cooking vessel under the acidic conditions of the water prehydrolysis. This fact needs to be taken into consideration when designing equipment used for hot-water extraction of wood chips.

**Table 4.** Metal Contents of Examined Pulps Before Oxygen Delignification

| Sample | Fe, ppm | Mn, ppm | Cu, ppm |
|---|---|---|---|
| Pulp 1 | 11.0 | 12.1 | 22.3 |
| Pulp 2 | 30.7 | 8.7 | 9.5 |
| Pulp 3 | 75.7 | 7.1 | 17.2 |

## The Effect of Prehydrolysis on Pulp Properties

Handsheet properties were evaluated for the bleached pulps at an ISO-brightness of 74% for pulps 1 and 2, and 72% for pulp 3. Figure 4 depicts the number of revolutions in a PFI-mill required to achieve a tensile index value of 70 Nm/g for the examined pulps. Tear index values at the corresponding tensile index for each pulp are presented above the columns.

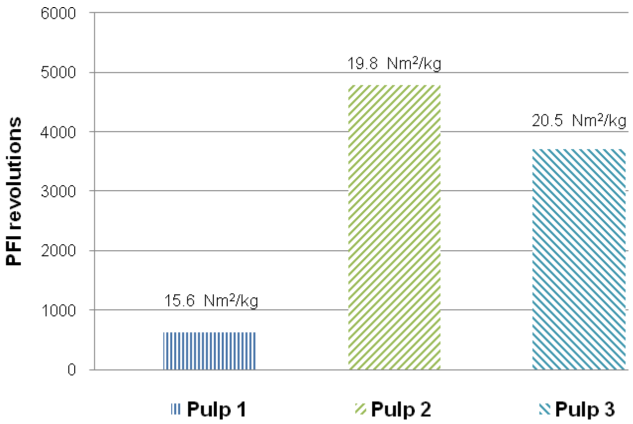

**Fig. 4.** Required number of revolutions in a PFI-mill in order to achieve a tensile index of 70 Nm/g. Tear index values at the corresponding tensile index are presented above each column. Respective densities for pulps 1, 2, and 3 after beating to a tensile index of 70 Nm/g were 705, 720, and 720 kg/m$^3$, respectively.

As Fig. 4 indicates, prehydrolyzed pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than unhydrolyzed pulp 1 to achieve a given tensile index value. This is in line with previous findings, since shorter beating times and less energy absorption in beating is a feature of kraft pulps having high hemicellulose content (Rydholm 1967; Vaaler et al. 2002; Young 1994). Hemicelluloses contribute significantly to the swelling tendency of fibers. With increased swelling, interfiber contact during beating increases promoting faster external fibrillation and hence better beating response. As reported by Yoon and van Heiningen (2008) regarding slower beating responses for hot-water pre-extracted kraft pulps, the relation between hemicellulose content and beating response has also been observed with low hemicellulose content pulps. The significant reduction in beating response and strength development might present problems in commercialization of prehydrolyzed pulps.

The prehydrolyzed pulps in this study exhibited higher tear index values with the same tensile index value as unhydrolyzed pulp, as can be seen in Fig. 4. Consequently, prehydrolyzed pulps had better strength potential (tensile index x tear index) than unhydrolyzed pulp. Strength potential values were plotted as a function of sheet density (not shown), and the highest strength potential (tensile index x tear index) for both unhydrolyzed and prehydrolyzed pulps was achieved approximately at density 700 kg/m$^3$. Table 5 presents values of pulp properties interpolated to the density value 700 kg/m$^3$.

**Table 5.** Properties of pulps 1, 2, and 3 at Density 700 kg/m$^3$. Values are Interpolated to the Given Density

| Property | Density [kg/m$^3$] | Pulp 1 | Pulp 2 | Pulp 3 |
|---|---|---|---|---|
| Cellulose/hemicellulose ratio | | 4.9 | 10.6 | 10.1 |
| Beating revolutions [-] | 700 | 525 | 2395 | 1585 |
| CSF [ml] | 700 | 684 | 668 | 677 |
| Tensile index [Nm/g] | 700 | 67.1 | 58.2 | 62.1 |
| Tear index [Nm$^2$/kg] | 700 | 16.2 | 22.6 | 23.9 |
| Tensile stiffness index [kNm/g] | 700 | 6.87 | 6.17 | 6.60 |
| Gurley air permeance [µm/Pas] | 700 | 37.6 | 42.5 | 42.1 |
| Light-scattering coefficient [m$^2$/kg] | 700 | 22.7 | 23.8 | 24.2 |
| Opacity [-] | 700 | 69.2 | 72.0 | 74.8 |

Table 5 shows that as approximately half of the hemicelluloses were removed by water prehydrolysis, pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than pulp 1 in order to reach the density level at which the highest value for strength potential was attained. Additional beating of pulps 2 and 3 led to lower pulp freeness (CSF), yet the tensile index of these pulps was lower than for pulp 1.

A decrease in tensile index and an increase in tear index are considered to be the main features of low hemicelluloses content pulps (Kettunen et al. 1982; Molin and Teder 2002; Rydholm 1967; Spiegelberg 1966). As can be seen in Table 5, these features were also observed in this study. Tensile stiffness index was also affected. Partial removal of hemicelluloses by prehydrolysis lowers the tensile stiffness index value. The tensile stiffness index is defined as the maximum angular coefficient in the stress-strain curve of the paper. The major factor affecting this angular coefficient is the amount of fiber-to-fiber bonding (Giertz and Rodland 1979); the stronger the fiber-to-fiber bonding, the higher the maximum angular coefficient. This leads to an assumption that fiber-to-fiber bonding in the fiber network is diminished in sheets made from prehydrolyzed pulp. Reduced fiber-to-fiber bonding has been reported to decrease tensile index values (Rydholm 1967) and increase tear index values (Bronkhorst and Bennett 2002). The decreased tensile index and increased tear index of this study would therefore also support the assumption that prehydrolysis reduces fiber-to-fiber bonding in the fiber network. Also Yoon and van Heiningen (2008) have suggested that the negative effects of hot-water pre-extraction on tensile strength of kraft pulps could be explained by the low interfiber bonding ability of the hemicellulose-poor pulps.

Prehydrolyzed pulps 2 and 3 formed sheets with a higher light-scattering coefficient (LSC), opacity and air permeability than unhydrolyzed pulp 1. The optical properties, LSC and opacity, were even better when prehydrolyzed pulp was cooked at a lower sulfidity level, 20% instead of 40%. Compact, narrow, and thick-walled fibers are known to form a porous paper that has high ability to scatter light.

Therefore, the dimensions of prehydrolyzed softwood fibers had likely changed compared to unhydrolyzed fibers, enabling more opaque, porous, and light-scattering sheets. Similar properties for paper sheets with various hemicellulose contents have also been reported by Hunger (1983) and Santos et al. (2008). Increased LSC and opacity also indicate decreased interfiber bonding in sheets made from prehydrolyzed pulps, since increasing interfiber bonding with fibrillar fines is known to have a negative effect on LSC (Luukko and Paulapuro 1999), and opacity is increased by decreasing interfiber bonding with debonding agents (Talaeipoor and Imani 2008). Therefore, differences in interfiber bonding are likely to be the main cause for the differences in the paper properties between prehydrolyzed and unhydrolyzed pulps.

## CONCLUSIONS

1. The cooking of prehydrolyzed chips is significantly faster than that of unhydrolyzed chips. To obtain similar kappa numbers at similar cooking temperatures, the prehydrolyzed chips require approximately 40% shorter cooking times.
2. Prehydrolysis at P-200 decreases the pulp yield on wood by approximately 7.2 percentage units.
3. The response to oxygen delignification is higher with prehydrolyzed chips, allowing cooking to be stopped at higher kappa numbers.
4. The same final brightness (74% ISO) in (O)DED-bleaching can be reached with lower chemical consumption when wood chips are prehydrolyzed prior to cooking and cooked with a similar sulfidity level.
5. Prehydrolyzed pulps require considerably more beating to reach a specific pulp freeness (CSF) or tensile index than unhydrolyzed pulp, but exhibit higher strength potential (tensile index x tear index) at given densities.

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# Publication III

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**Design and simulation of an organosolv process for bioethanol production**

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ORIGINAL ARTICLE

# Design and simulation of an organosolv process for bioethanol production

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**Abstract** Organosolv pulping can be used as a pretreatment step in bioethanol production. In addition to ethanol, organosolv pulping allows for the production of a pure lignin product and other co-products. Based on publicly available information, conceptual process design and simulation model were developed for an organosolv process. The simulation model was used to calculate the mass and energy balances and approximate fossil-based carbon dioxide ($CO_2$) emissions for the process. With a hardwood feed of 2,350 dry metric tons (MT) per day, 459 MT/day (53.9 million gallons per year) of ethanol was produced. This corresponded to a carbohydrate to ethanol conversion of 64 %. The production rates of lignin, furfural, and acetic acid were 310, 6.6, and 30.3 MT/day, respectively. The energy balance indicated that the process was not energy self-sufficient. In addition to bark and organic residues combusted to produce energy, external fuel (natural gas) was needed to cover the steam demand. This was largely due to the energy consumed in recovering the solvent. Compared to a dilute acid bioethanol process, the organosolv process was estimated to consume 34 % more energy. Allocating all emissions from natural gas combustion to the produced ethanol led to fossil $CO_2$ emissions of 13.5 g per megajoule (MJ) of ethanol. The total fossil $CO_2$ emissions of the process, including also feedstock transportation and other less significant emission sources, would almost certainly not exceed the US Renewable Fuel Standard threshold limit (36.5 g $CO_2$/MJ ethanol).

**Keywords** Organosolv · Pretreatment · Bioethanol · Mass and energy balances · Simulation · Carbon dioxide

**Abbreviations**

| | |
|---|---|
| AFEX | Ammonia fiber explosion |
| $CO_2$ | Carbon dioxide |
| DP | Furfural degradation products |
| EtOH | Ethanol |
| F | Furfural |
| GHG | Greenhouse gas |
| $H_2SO_4$ | Sulfuric acid |
| HCl | Hydrochloric acid |
| HMF | 5-Hydroxymethylfurfural |
| $k_i$ | Kinetic coefficients |
| LMW | Low molecular weight |
| LTW | Liquid-to-wood ratio |
| MT | Metric ton |
| NaOH | Sodium hydroxide |
| NREL | National Renewable Energy Laboratory |
| NRTL | Non-random two-liquid |
| NRTL-HOC | Non-random two-liquid-Hayden-O'Connel |
| SPORL | Sulfite pretreatment to overcome lignocelluloses recalcitrance |

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| | |
|---|---|
| TOPO | Trioctyl phosphine oxide |
| *v*/*v* | Volume/volume (volume concentration) |
| wt% | Mass percentage |
| WWT | Wastewater treatment |
| X | Monomeric xylose |
| XO | Oligomeric xylan |

## 1 Introduction

Processing of abundant and renewable lignocellulosic biomass sources to biofuels has generally been seen as a way to address the problem of depleting fossil fuel sources and their contribution to greenhouse gas emissions (see e.g., [1]). This rationale has led to the development of different biorefinery concepts (see e.g., [2]) for the conversion of biomass to different fuels and products in fully integrated production facilities. Ethanol already has an established market as a liquid biofuel, with an annual global production of approximately 22.3 billion gallons [approximately 67 million metric tons (MT)] in 2011 mainly from sugar and starch crops [3]. It is of significant current interest also as a potential second-generation biofuel produced from lignocellulosic biomass.

The production of ethanol from lignocellulosic material through a biochemical route consists of four major steps: pretreatment, hydrolysis, fermentation, and product stream purification. In its native state, lignocellulosic material is recalcitrant to efficient direct hydrolysis of cellulose carbohydrate to glucose monomer due to the physicochemical and structural composition of the material [4]. Pretreatment refers to the mechanical, physical, chemical, and/or biological treatments to reduce the particle size of the material and disrupt its cell structure to make it more accessible to chemical or enzymatic hydrolysis treatments. More specifically, the aims of pretreatment are typically the hydrolyzation of hemicelluloses and reduction of crystallinity and degree of polymerization of cellulose, to facilitate the subsequent enzymatic hydrolysis of cellulose. After the pretreatment stage, the carbohydrates are converted to monomeric sugars in the hydrolysis step utilizing either enzymes or acids, and the sugars are then fermented to ethanol. Several different pretreatment methods have been proposed, including uncatalyzed and acid catalyzed steam explosion, liquid hot water, dilute acid, alkaline, AFEX, and organosolv [1, 5, 6]. Being one of the most expensive processing steps in the conversion of lignocellulosic material to ethanol [5], the development and selection of pretreatment method has a critical role in making the production of lignocellulosic ethanol feasible and cost-effective.

Organosolv pulping, in which organic solvents are used to degrade and dissolve lignin from lignocellulosic material, was originally designed and conceived as a pulping process for the production of paper pulp (see e.g., [7, 8]). More recently, it has gained interest as a potential pretreatment method for lignocellulosic biomass for bioethanol production, mainly because the delignified organosolv pulps have been found to have a good response to enzymatic hydrolysis and the organosolv process allows for the recovery of several co-products (see e.g., [9, 10]).

Despite its perceived benefits, the usage and recovery of solvents have been assumed to render the organosolv process more complex and potentially more expensive pretreatment method than most other methods. For example, due to cumbersome washing arrangements of organosolv pulp after cooking, high energy consumption in distillation, and problems with sealing of pulping equipment to avoid fire and explosion hazards related to volatile organic components, Zhao et al. [11] estimated the organosolv process to be too expensive as a pretreatment method for bioethanol production. Also, Zheng et al. [6] estimated the organosolv pretreatment process to be too expensive and complex. This perceived high cost of organosolv pulping, or the extent to which the recovery of co-products could offset this cost, was not, however, analyzed in more detail in the two reviews.

A wide array of organic solvents have been proposed and tested as pulping agents for organosolv pulping, including alcohols (e.g., methanol and ethanol), organic acids (e.g., formic acid and acetic acid), phenol, cresols, ethyl acetate, amines and amine oxides, ketones, and dioxane [12]. Organosolv pulping can be either catalyzed by acids or auto-catalyzed (catalyzed by acetic acid cleaved from hemicellulose acetyl groups during pulping). Alkaline organosolv systems, where organic solvent is used in combination with alkali, have also been proposed [13]. In acid and auto-catalyzed organosolv pulping, lignin is cleaved and dissolved in the organic solvent [13], and the main pathways of lignin breakdown are the acid-catalyzed cleavage of β-O-4 linkages and ester bonds [14]. Carbohydrates undergo hydrolysis reactions and dissolve in the cooking liquor as oligomeric and monomeric sugars and possibly react further to sugar degradation products. The dissolved lignin can be precipitated from the pulping liquor as a high-purity, low molecular weight, and narrow molecular weight distribution lignin product by diluting the pulping liquor with water [15]. The use of pure organosolv lignin has been considered in many applications, including phenolic resins, epoxy resins, and polyurethane foams [15, 16]. In addition to lignin, several other co-products can be recovered from the aqueous stream containing pulping products of hemicelluloses, including sugars, acetic acid, and furfural (see e.g., [9, 17]).

Using different organic solvents and raw materials, numerous experimental studies have been published on organosolv. For example, Muurinen [12] reviewed over

900 papers on organosolv pulping. Traditionally, organosolv pulping has mainly been seen as a pulping method for paper pulp production in these studies. As a pretreatment method prior to enzymatic hydrolysis, especially sulfuric acid-catalyzed ethanol pulping has been studied in the recent literature (e.g., [9, 10, 14, 18–26]).

In addition to laboratory studies, a few process design, process analysis, and simulation studies on organosolv processes have also been published. For example, Furlan et al. [27] presented a simulation study of an integrated first- and second-generation bioethanol production process where both the sugarcane juice and bagasse were converted to ethanol. The second-generation process was based on organosolv pretreatment. They varied the amount of bagasse burnt in the combustor and found this variation to affect the internal heat demand and electricity output of this integrated sugarcane bioethanol process considerably. Dias et al. [28] simulated a similar integrated sugarcane process. They compared a first-generation process to different integrated processes where the second-generation process was based either on sulfur dioxide catalyzed steam explosion, alkaline hydrogen peroxide, or organosolv pretreatment with varying dry solids contents in enzymatic hydrolysis and fermentation times. At a dry solids content of 5 % in the hydrolysis stage and a fermentation time of 24 h, both the ethanol and surplus electricity production of the organosolv process were found to be lower than that of to the steam explosion process, but the internal rates of return were similar. Ojeda et al. [29] presented the simulation, design as well as energy and life cycle analyses on second-generation bioethanol processes based on diluted acid, liquid hot water, acid catalyzed steam explosion, and organosolv pretreatments. Organosolv-based bioethanol process was found to have a high energy demand, resulting in the highest life cycle emissions. García et al. [30] presented a simulation and heat integration study on an ethanol organosolv pulping process. Zhu and Pan [31] compared the energy consumption of steam explosion, organosolv, and sulfite pretreatment to overcome lignocelluloses recalcitrance (SPORL) pretreatments. The exact order depended on the adopted assumptions, but the organosolv pretreatment was generally found to have lower energy consumption than steam explosion and higher energy consumption than SPORL pretreatment. Vila et al. [32] presented a preliminary process design and simulation study on acetosolv pulping of eucalyptus, which uses concentrated acetic acid with hydrochloric acid as a catalyst, and discussed the recovery of solvent, lignin, furfural, and hemicellulosic sugars in the process. Botello et al. [33] studied the recovery of lignin, furfural, and solvent in ethanol and methanol organosolv processes. Parajó and Santos [34] provided a techno-economic study on the acid-catalyzed acetic acid pulping of *Eucalyptus globulus* wood for the production of paper pulp and co-products. They calculated mass and energy balances for a proposed process flowsheet and analyzed the economic feasibility as well as the effect of pulping conditions and the price of pulp, raw material, and co-products on the feasibility. A summary of the studies described in this paragraph is presented in Table 1. A more detailed discussion on the existing literature on conceptual process design and simulation studies of organosolv processes can be found in a recent review by Li et al. [35].

As discussed above, several process design and simulation studies on organosolv processes have been presented in the literature. However, no comprehensive studies on the process design and simulation of complete organosolv biorefinery systems including flowsheets and mass and energy balances of both the pretreatment, recovery of lignin and other co-products, and ethanol production are known to us. In this study, the simulation and conceptual process design of an acid-catalyzed ethanol organosolv pulping process for the production of bioethanol through enzymatic hydrolysis and fermentation will be developed. In addition to ethanol, the technical aspects of the production of co-products, namely lignin, acetic acid, and furfural, will be analyzed. Detailed flowsheets and mass and energy balances will be provided for the complete multi-product organosolv biorefinery. Also the approximate fossil-based carbon dioxide ($CO_2$) emissions of the process will be analyzed. As the organosolv pretreatment process has been considered relatively complex and potentially expensive in the literature, its energy consumption and ethanol production will be compared to a more standard dilute acid pretreatment/enzymatic hydrolysis bioethanol production process presented in a recent National Renewable Energy Laboratory (NREL) technical report [36]. To enable a justifiable comparison, processes downstream of the pretreatment process as well as auxiliary processes were assumed similar to those of the NREL study whenever applicable. The comprehensive technical analysis presented in this paper provides a sound basis for an economic assessment of the organosolv process.

## 2 Materials and methods

### 2.1 Process overview

Using literature sources and Aspen PLUS™ 7.1 [37] simulation software, a simulation model of an ethanol organosolv process was created. The pulping section of the process flowsheet was constructed following partially the works of Agar et al. [38] and Pan et al. [9] on ethanol organosolv pulping. The NREL technical report on

**Table 1** Summary of the organosolv process design, process analysis, and simulation studies reviewed in this paper

| Reference | Feedstock | Type of solvent in organosolv cooking | Specified products produced in the process |
|---|---|---|---|
| [27] | Sugarcane bagasse | Ethanol–water, washing of the pulp with NaOH | Ethanol both from cellulosic and hemicellulosic sugars, lignin combusted |
| [28] | Sugarcane bagasse and trash | Ethanol–water with different catalysts (apparently $H_2SO_4$ and NaOH) | Ethanol from cellulosic sugars, hemicellulosic sugars biodigested for biogas production and further combusted, lignin combusted |
| [29] | Sugarcane bagasse | Ethanol–water with $H_2SO_4$ as a catalyst | Ethanol both from cellulosic and hemicellulosic sugars |
| [30] | Lignocellulosic non-wood feedstock | Ethanol–water | Cellulosic solid fraction (pulp), concentrated stream enriched in hemicellulosic sugars, lignin |
| [31] | Lodgepole pine | Ethanol–water with $H_2SO_4$ as a catalyst (based on [19]) | Cellulosic and hemicellulosic sugars |
| [32] | *Eucalyptus globulus* | Acetic acid–water with HCl as a catalyst | Cellulosic pulp, concentrated stream enriched in hemicellulosic sugars, lignin, furfural |
| [33] | *Eucalyptus globulus* | Ethanol–water and methanol–water | Cellulosic pulp, stream enriched in hemicellulosic sugars, lignin |
| [34] | *Eucalyptus globulus* | Acetic acid–water with HCl as a catalyst | Cellulosic pulp, hemicellulosic sugars, lignin, furfural |

lignocellulosic ethanol [36] was used in creating the models of subsequent enzymatic hydrolysis and fermentation as well as all auxiliary processes. In the assumed process, debarked hardwood chips are delignified in organosolv cooking, and the resulting pulp is washed and sent to enzymatic hydrolysis and fermentation steps. The residual cooking liquor is flashed to reduce its temperature and recover part of its heat and solvent content back to pulping. The cooled liquor is then sent to a post-hydrolysis reactor for the hydrolysis of sugar oligomers to monomers, after which it is further flashed and diluted with water to precipitate lignin. Ethanol is then recovered in distillation columns, with recovery of furfural as a side-draw. The aqueous bottom stream is then concentrated by evaporation and acetic acid is recovered from the evaporator condensates by extraction. Low molecular weight (LMW) lignin is separated in decantation and extraction stages, and the hemicellulosic sugars are sent to fermentation after a pH adjustment step. Figure 1 presents a block diagram of the modeled ethanol organosolv biorefinery. More detailed flowsheets are presented in Electronic supplementary material (ESM) Fig. 1S, 2S, 3S, and 4S.

To enable comparison of the organosolv process with the abovementioned NREL process [36], an intake of 2,000 dry MT of debarked hardwood chips per day was assumed in the model. Bark content and debarking and screening losses were assumed to total 15 %, resulting in a total raw wood consumption of approximately 2,350 dry MT/day. The moisture content of the feedstock was assumed to be 50 %. As will be discussed below, results of Pan et al. [10] on the organosolv cooking of hybrid poplar were followed in determining the mass balance over cooking. The hardwood in question in this study was therefore implicitly assumed to be hybrid poplar.

## 2.2 Process simulation

Aspen PLUS™ V7.1 was used in creating a simulation model of the process concept. NRTL (non-random two-liquid) property method, based on the NRTL model for the liquid phase activity coefficients and ideal gas equation for the vapor phase, was used as the main property method. To take into account the dimerization of carboxylic acids in the vapor phase, NRTL-HOC (Hayden-O'Connel equation of state for the vapor phase) was used in flash and evaporation units where carboxylic acids were present. The binary parameters for the NRTL activity coefficient model were retrieved from Aspen PLUS™ VLE-LIT and LLE-Aspen databanks. For binary pairs for which parameters were available, LLE-Aspen was used in liquid–liquid extraction units and other occasions where two liquid phases were expected to appear. VLE-LIT was used in other units. The NREL report [36] was followed in choosing components for the Aspen model, with Aspen native components used when available.

## 2.3 Conceptual process design and process description

### *2.3.1 Pretreatment and lignin recovery*

The cooking process was assumed to be continuously operated. In determining the mass balance over the cooking process, results and conditions of laboratory batch cooking experiments of Pan et al. [10] for cooking of hybrid poplar were used.

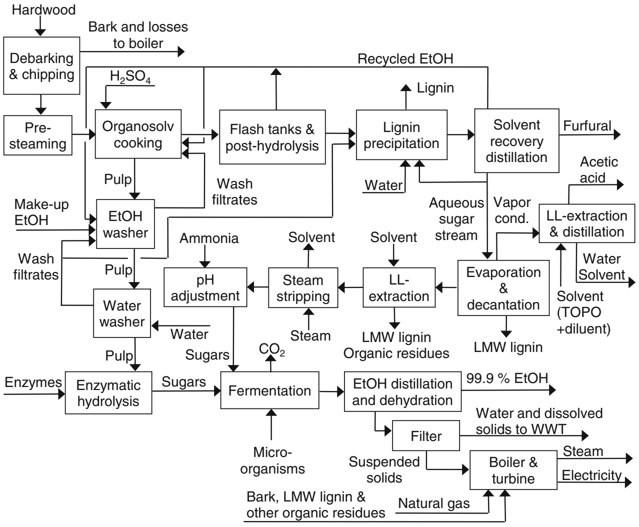
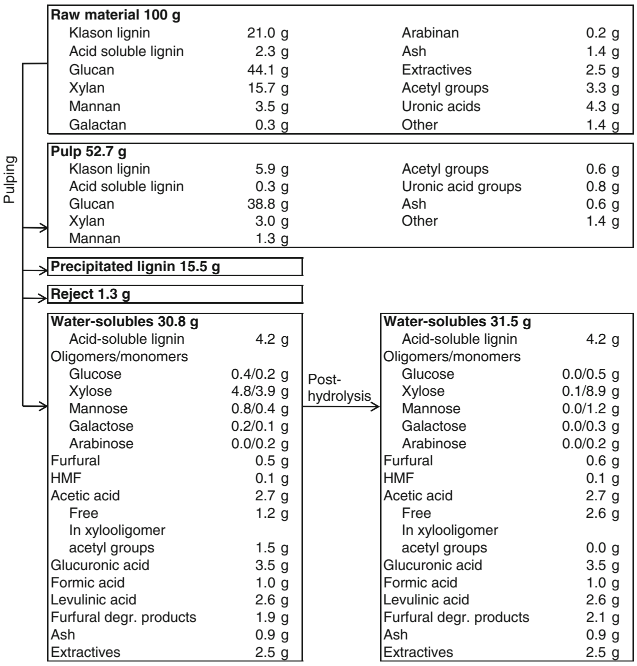


**Fig. 1** Block diagram of the modeled ethanol organosolv biorefinery

Specifically, the conditions of 180 °C, 60 min, 1.25 % sulfuric acid on dry wood, and 50 % (*v*/*v*) ethanol concentration ("center point conditions" of that article) were followed. Unlike in their experiments where the liquid-to-wood ratio (LTW) was 7, LTW was set to 5 in this model to decrease the energy consumption in solvent recovery. This modification was considered justifiable and technically reasonable since Goyal et al. [39] reported only slight decreases in delignification with decreasing LTWs, and because conventional Kraft cooking processes are typically run with even lower LTWs.

Since the closure of the mass balance presented for the abovementioned center point conditions in Figure 2 of Pan et al. [10] was approximately 90 %, certain assumptions were made to close the balance. In their paper, extractives, ash, methyl glucuronic acid, and acetate side group contents of the raw material were not measured. The contents of these were estimated based on Sannigrahi et al. [40]. The raw material carbohydrate content, presented as sugars in the article of Pan et al. [10] (pentoses and hexoses), was here converted to carbohydrate basis (pentosans and hexosans). The rest of the raw material was assumed to be other, unspecified material. In the water-soluble product stream, the acid soluble lignin content was slightly decreased compared to that of Pan et al. [10] since part of it was assumed to be extractive components. Further, as can be seen in Fig. 2, the combined lignin content of products exceeds that of the raw material. This was assumed to be explained by lignin condensed on carbohydrates. In the simulation model, this balance of lignin was modeled as "lignin-like carbohydrates," carbohydrates rendered nonreactive to enzymatic hydrolysis and fermentation due to condensation of lignin and grouped as "lignin" in mass balances. Pan et al. [10] measured 71 % of mannose and 58 % of xylose present in the water-soluble stream to be in oligomeric form. In the present study, this finding was extended assuming that 71 % of all hexose sugars in the water-solubles stream would be present in oligomeric form. All of the arabinose in the water-solubles stream was assumed to be in monomeric form. The oligomeric sugars present in the water-solubles stream were assumed to be hydrolyzed to monomeric sugars in a separate post-hydrolysis step that is described in more detail in a separate paragraph below. The reject fraction (incompletely defiberized wood material) was assumed to consist entirely of carbohydrates. Overall carbohydrate mass balances were then calculated taking into account the abovementioned assumptions regarding the carbohydrate contents of the reject and lignin fractions as well as the contents of carbohydrates and carbohydrate-derived components [sugars, furfural, 5-hydroxymethylfurfural (HMF)] in the raw material, pulp, and water-soluble fractions as reported by Pan et al. [10]. Residual carbohydrates unaccounted for in the balance were assumed to have reacted into components that are further down the thermal decomposition pathway of sugars and were not measured by Pan et al., with residual hexosans assumed to be degradation products of HMF, namely formic and levulinic acid and residual pentosans unidentified degradation products of furfural. These assumptions are in line with Pan et al. [10] who suggested that the relatively low carbohydrate recovery (84 %) of their study is an indication of further degradation of furfural and HMF. See Fig. 2 for the assumed composition of the raw material, pulp, and aqueous streams.



**Raw material 100 g**

| | | | |
|---|---|---|---|
| Klason lignin | 21.0 g | Arabinan | 0.2 g |
| Acid soluble lignin | 2.3 g | Ash | 1.4 g |
| Glucan | 44.1 g | Extractives | 2.5 g |
| Xylan | 15.7 g | Acetyl groups | 3.3 g |
| Mannan | 3.5 g | Uronic acids | 4.3 g |
| Galactan | 0.3 g | Other | 1.4 g |

**Pulp 52.7 g**

| | | | |
|---|---|---|---|
| Klason lignin | 5.9 g | Acetyl groups | 0.6 g |
| Acid soluble lignin | 0.3 g | Uronic acid groups | 0.8 g |
| Glucan | 38.8 g | Ash | 0.6 g |
| Xylan | 3.0 g | Other | 1.4 g |
| Mannan | 1.3 g | | |

**Precipitated lignin 15.5 g**

**Reject 1.3 g**

**Water-solubles 30.8 g**

| | |
|---|---|
| Acid-soluble lignin | 4.2 g |
| Oligomers/monomers | |
| Glucose | 0.4/0.2 g |
| Xylose | 4.8/3.9 g |
| Mannose | 0.8/0.4 g |
| Galactose | 0.2/0.1 g |
| Arabinose | 0.0/0.2 g |
| Furfural | 0.5 g |
| HMF | 0.1 g |
| Acetic acid | 2.7 g |
| Free | 1.2 g |
| In xylooligomer acetyl groups | 1.5 g |
| Glucuronic acid | 3.5 g |
| Formic acid | 1.0 g |
| Levulinic acid | 2.6 g |
| Furfural degr. products | 1.9 g |
| Ash | 0.9 g |
| Extractives | 2.5 g |

**Water-solubles 31.5 g**

| | |
|---|---|
| Acid-soluble lignin | 4.2 g |
| Oligomers/monomers | |
| Glucose | 0.0/0.5 g |
| Xylose | 0.1/8.9 g |
| Mannose | 0.0/1.2 g |
| Galactose | 0.0/0.3 g |
| Arabinose | 0.0/0.2 g |
| Furfural | 0.6 g |
| HMF | 0.1 g |
| Acetic acid | 2.7 g |
| Free | 2.6 g |
| In xylooligomer acetyl groups | 0.0 g |
| Glucuronic acid | 3.5 g |
| Formic acid | 1.0 g |
| Levulinic acid | 2.6 g |
| Furfural degr. products | 2.1 g |
| Ash | 0.9 g |
| Extractives | 2.5 g |

**Fig. 2** Schematic dry solids mass balance over cooking, post-hydrolysis, and lignin separation assumed in the model (figure layout partially adopted from [10], balances based on [10, 40, 41])

In the cooking process, the debarked chips were first assumed to be presteamed with low pressure steam in a steaming bin at atmospheric pressure, then fed through a metering screw and rotary valve feeder, heated with direct steam to approximately 130 °C, mixed with the cooking liquor and sulfuric acid in a high pressure sluice, pressurized to the cooking temperature, and fed to the top of the digester, as outlined in the work of Agar et al. [38]. The digester was assumed to be continuously operated with concurrent and countercurrent cooking zones and a washing zone. The cooking liquor was heated to the maximum cooking temperature of 180 °C by circulating liquor in heat exchangers and heating it with high pressure steam. The pressure in the digester was set to 2 MPa. Spent cooking liquor was assumed to be extracted at maximum cooking temperature at the midsection of the digester. The amount of extracted liquor was set to obtain a dry solids content of 30 % solids content in the digester after extraction. The pulp and the residual liquor in the digester were then assumed to be cooled to approximately 130 °C with heat exchangers, and diluted to approximately 10 % solids content and cooled to approximately 85 °C with washer filtrates. The pulp was then discharged from the bottom of the digester through a pressure reduction valve to defiberize it. The heat from the heat exchangers used to cool the cooking liquor was assumed to be used to preheat the cooking liquor fed to the digester. The yield on wood in pulping and the residual lignin content of the pulp were 52.7 and 11.7 %, respectively.

After pulping, the pulp stream was fed to a washing stage. The washing was assumed to be carried out countercurrently to recover heat from the pulp stream back to the recycled cooking liquor. To avoid lignin condensation reactions after pulping, the pulp was first washed with ethanol containing wash liquors to remove dissolved lignin (EtOH washer in Fig. 1). The pulp was then washed with water to recover ethanol from the pulp (water washer in Fig. 1). The ethanol and water washers were assumed to be pressure diffuser and medium consistency drum displacer washer, respectively. The ethanol washer was assumed to have four washing stages and inlet and outlet consistencies of 10 %. The water washer was assumed to have 14 washing stages and inlet and outlet consistencies of 10 and 16 %, respectively. Wash liquor to the water washer was set to obtain a dilution factor of 2. This dilution factor is defined as the difference of wash liquor flow and liquor flow leaving with the washed pulp per dry mass flow of pulp to washing. The wash filtrate from the water washing step was used partially in the ethanol washer, along with part of the recycled ethanol from the distillation and flashing steps and make-up ethanol. The dilution factor in the ethanol washer was 1.7. The ethanol concentration in the combined washing liquor to the ethanol washer was approximately 52 % (*v*/*v*). To obtain the required ethanol concentration of 50 % (*v*/*v*) in the digester, part of the wash filtrate from the water washer was fed to the lignin precipitation and subsequent ethanol recovery distillation steps to increase the overall ethanol concentration of the cooking liquor. After washing, the pulp was assumed to contain low enough amount of inhibitors not to require a separate conditioning stage. The pulp was pumped through a screen to separate the reject fraction and fed to the enzymatic hydrolysis stage. The rejects were assumed to be separated at a dry solids content of 30 wt% and fed to burning.

The spent pulping liquor from cooking was assumed to be flashed to a temperature of approximately 135 °C after pulping and before feeding it to a post-hydrolysis vessel for approximately 1 h to hydrolyze the sugar oligomers to monomers for fermentation. The flash vapor was set to be condensed in the reboiler of the higher pressure ethanol recovery distillation column (see subsection 2.3.2) to provide energy for distillation, as suggested in the work of Agar et al. [38], and then recycled back to cooking.

As stated above, oligomeric sugars present in the spent cooking liquor were converted to monomeric sugars in a separate post-hydrolysis step. The reactions taking place in the step were modeled using a kinetic model presented by Garrote et al. [41] for post-hydrolysis of autohydrolysis liquors in a dilute acid hydrolysis, with the kinetics of the hydrolysis of oligomeric xylan (XO) to monomeric xylose (X), the dehydration of xylose to furfural (F), and the degradation of furfural to degradation products (DP) assumed to follow a series of consecutive, irreversible pseudo first-order reactions, as presented by equation

$$\mathrm{XO} \overset{k_1}{\rightarrow} \mathrm{X} \overset{k_2}{\rightarrow} \mathrm{F} \overset{k_3}{\rightarrow} \mathrm{DP} \tag{1}$$

No acid was assumed to be added to the post-hydrolysis stage, leaving a sulfuric acid concentration of 0.3 wt% in the stage with residual acid from pulping. Kinetic coefficients reported by Garrote et al. [41] for post-hydrolysis at a temperature of 135 °C and a sulfuric acid concentration of 0.5 wt% were adjusted for differences in sulfuric acid concentrations based on the dependence of pre-exponent on acid concentration described by Garrote et al. The kinetic coefficients $k_1$, $k_2$, and $k_3$ were calculated to be 3.74, 0.046, and 0.22 $h^{-1}$, respectively. Other sugar oligomers and monomers were assumed to follow similar kinetics with the same kinetic coefficients, with hexoses dehydrating to HMF, then degrading further to formic and levulinic acids.

After post-hydrolysis, the pulping liquor was further flashed to recover heat and solvent before diluting the liquor for lignin precipitation. The flashing was carried out in two stages, first at approximately 170 kPa to provide steam for the evaporation of the hemicellulosic sugar stream, and then at 70 kPa. The last flashing stage was carried out at reduced pressure to increase the evaporation of ethanol and decrease the amount of dilution water needed in the precipitation of lignin, as outlined in the work of Agar et al. [38]. The pressure was set to obtain an ethanol concentration of 30 % (*v*/*v*) after flashing, a concentration which was assumed high enough to avoid premature lignin precipitation [38]. The pulping liquor was then diluted with recycled bottoms stream from the distillation columns to an ethanol concentration of approximately 15 % (*v*/*v*) and cooled to 50 °C. Under these conditions, the relative amount of dissolved lignin precipitated from the pulping liquor was assumed to be 79 %, the same amount as in the study of Pan et al. [10] at an ethanol concentration of 12.5 % (*v*/*v*) (50 % (*v*/*v*) pulping liquor diluted with three volumes of water). At similar ethanol concentration of 15 % (*v*/*v*) but at a lower temperature of 23 °C, Ni and Hu [42] measured approximately 90 % of hardwood organosolv lignin precipitated. It was therefore considered reasonable to assume 79 % of lignin dissolved in cooking to be precipitable at 15 % (*v*/*v*) ethanol concentration. The lignin solids were then assumed to be separated with a filter [38] and subsequently dried in a spray dryer. Other alternatives to recover the precipitated lignin include centrifugation [38] and dissolved air flotation [43]. These were, however, not considered in this study. Natural gas was assumed to be used as an energy source in drying. The filtrates were recycled back to the lignin precipitation stage. Figure 2 presents a schematic dry solids mass balance over cooking, post-hydrolysis, and lignin separation. The actual mass balance in the simulation model is slightly different due to recycle, splitting, and mixing of streams between stages. A flowsheet containing the cooking, pulp washing, post-hydrolysis, and lignin recovery stages is presented in ESM Fig. 1S.

### 2.3.2 Solvent and furfural recovery

After the dilution of spent pulping liquor and lignin precipitation, ethanol was recovered from the liquor back to the cooking process by distillation. To reduce steam demand, the distillation was assumed to be carried out in two heat-integrated distillation columns with different operating pressures. The feed stream was assumed to be split and sent to both columns. The pressure in the lower pressure column (18 kPa) was set so that the temperature of its condenser was approximately 40 °C, allowing for the use of water at approximately 30 °C in cooling. The pressure of the higher pressure column (100 kPa) was set so that the temperature of its condenser (approximately 78 °C) was approximately 20 °C higher than that in the reboiler of the lower pressure column (approximately 58 °C), allowing for the utilization of heat from the condenser of the higher pressure column in the reboiler of the lower pressure column. Ninety percent of the heat from the condenser was assumed recoverable, and the split of the feed stream to the two columns was set to match the heat duties of the condenser and reboiler of the columns. To obtain a high ethanol recovery of over 99.9 % and a high ethanol concentration of approximately 91 % (*v*/*v*) in the distillate, and with a distillate to feed ratio of approximately 0.14, the minimum number of equilibrium stages in the distillation columns was identified to be approximately 10. The actual number of stages was set to 25 and the reflux ratio to approximately 2.3.

Furfural, which creates a minimum-boiling heterogeneous azeotrope with water, was set to be recovered as a liquid side-draw from plate 9 in both columns. The side-draw was then assumed to be cooled to a temperature of 40 °C and fed to a decanter to separate a furfural-rich organic phase. The aqueous phase was recycled back to the ethanol recovery distillation columns, and the furfural-rich stream was fed to a furfural purification column to produce pure furfural as a bottom product. The number of equilibrium stages was set to 12 and reflux ratio to approximately 0.2 in the furfural purification column. The distillate was fed back to the solvent recovery columns.

To reduce the amount of water in the system and increase the dry solids content of the bottoms streams from the distillation columns, the bottoms streams were used in the lignin precipitation step. Based on the kinetic data of Garrote et al. [41], the degradation of sugar monomers was assumed to be minor in temperatures and acid concentrations prevalent after pulping and post-hydrolysis, thus enabling this partial sugar stream recycle. All of the bottoms of the lower-pressure column and part of the bottoms of the higher-pressure column were set to be recycled back to lignin precipitation to achieve an ethanol concentration of 15 % (*v*/*v*). A flowsheet containing the ethanol and furfural distillation stages is presented in ESM Fig. 1S.

### *2.3.3 Conditioning of the hemicellulosic sugar stream*

As suggested in the work of Agar et al. [38], the sugar stream was assumed to be evaporated to increase the dry solids content of the stream which was consequently assumed to allow for the separation of soluble LMW lignin. To save live steam and to minimize the evaporation of less volatile components, which might make the downstream separation and purification of acetic acid and recovery of extractant more difficult, the evaporation was carried out at low temperature and pressure with steam from flashing of the cooking liquor and with distillate from the ethanol product stream rectification column. The evaporation was carried out in a four-effect evaporation train to yield a sugar stream with a moisture content of approximately 44 wt%. With this moisture content after evaporation, the ethanol concentration produced by fermentation did not exceed 60 g/L, an ethanol tolerance limit of *Zymomonas mobilis* reported in the NREL study [36]. Between stages 2 and 3, at a moisture content of approximately 85 wt%, the LMW lignin was assumed to form a tarry organic phase that could be separated by decantation [38]. The decantation was assumed to separate 60 % of LMW lignin at a solids content of 70 %. The LMW lignin fraction was then assumed to be burned in the boiler.

After evaporation, the aqueous stream was assumed to be extracted with furfural in a counter-current extraction column to separate the residual LMW lignin from the stream, as presented in the work of Agar et al. [38]. As it reduces the content of inhibitory soluble lignin, the extraction step was assumed to be beneficial before fermentation. The step could, however, probably be omitted, especially if the extracted LMW lignin is not utilized. A recent Lignol patent [44] does not mention extraction as an option to treat the hemicellulosic stream.

Agar et al. [38] report furfural to be an excellent solvent for extracting LMW lignin, extracting over 70 % of lignin in a single extraction step, apparently with a 1:1 solvent volume ratio but without specifying the exact composition of the aqueous feed stream. Using vanillin as the model compound for LMW lignin and the modeled composition data of the aqueous hemicellulosic stream after evaporation, Aspen PLUS™ predicts approximately 86 % of residual LMW lignin to be extracted in a single step with a solvent volume ratio of 1:1. This implies that Aspen PLUS™ reasonably predicts the behavior of soluble lignin in extraction, and was thus used in modeling the extraction step. The extraction step was modeled as a four-stage extraction, and the solvent feed was set to obtain a soluble lignin separation of approximately 89 %, resulting in a solvent to feed volume ratio of approximately 0.57:1. With 89 % of lignin extracted, the soluble lignin content in fermentation would be below 0.5 g/L, which was assumed low enough not to cause inhibition (see e.g., Palmqvist and Hahn-Hägerdal [45] on the effect of phenolic compounds in fermentation). HMF was assumed to behave similarly to furfural in extraction, resulting in a HMF concentration of approximately 0.1 g/L in fermentation, assumed noninhibitory [46]. Other assumptions were such that furfural degradation products behave similarly to furfural in the extraction, 10 % of monomeric and oligomeric sugars are lost in the extraction, and the extraction of other components was set according to the Aspen PLUS™ predictions.

The raffinate from extraction, containing approximately 47 wt% water, 14 wt% furfural, and most of the sugars, was then assumed to be steam stripped to recover furfural. The Kremser shortcut method was used to approximate the number of stages in the stripping column as six, and the amount of low pressure steam was then set to obtain a furfural recovery of approximately 99 %, resulting in a furfural concentration in fermentation of well below 0.5 g/L, which was assumed noninhibitory [46]. The vapor flow from the stripping column was used to preheat the stream fed to the higher pressure solvent recovery distillation column and then the stream fed to the stripping column. After condensing and cooling the stream down to a temperature of 40 °C, it was split as a furfural-rich and water-rich phase in a decanter. The furfural-rich layer was assumed to be recycled back to extraction and the water-rich layer to the stripping column. The extract from extraction, containing approximately 21 wt% water, 40 wt% furfural, and most of the LMW lignin, was sent to a vacuum distillation column to recover furfural as a distillate, which was then recycled back to extraction. The bottoms stream, containing mainly LMW lignin and high-boiling pulping side products, levulinic acid and HMF, was sent to combustion. The vacuum distillation column (8 kPa) was modeled with five stages and a reflux ratio of approximately 0.6.

After the extraction step, the aqueous raffinate stream was assumed to be conditioned with ammonia to a pH of approximately 5 before fermentation, as outlined in the NREL study [36]. Here, the amount of ammonia needed in neutralization was simply set assuming a quantitative conversion of acids (acetic, formic, levulinic, and sulfuric acids) to ammonium salts. After the partial removal of LMW lignin, furfural, HMF, and other possible inhibitors and neutralization of the stream, the aqueous hemicellulosic sugar stream was assumed fermentable and was fed to the fermentation stage. A flowsheet containing the evaporation, extraction of lignin, steam stripping and vacuum distillation of furfural, and neutralization of the hemicellulosic stream stages is presented in ESM Fig. 2S.

Instead of fermenting the hemicellulosic sugars to ethanol, also other end-uses, such as the production of furfural [38], biogas [44], or xylitol [17], could be considered for the predominantly xylose-containing hemicellulosic stream. These were, however, not considered in this study.

### 2.3.4 Acetic acid recovery

Relatively volatile acetic and formic acids will partially accumulate in the evaporator train vapor condensates. They were assumed to be recovered from the condensates by extraction with trioctyl phosphine oxide (TOPO) in an undecane diluent, as outlined in the patent of Kanzler and Schedler [47] for the production and recovery of furfural, acetic acid, and formic acid from spent sulphite cooking liquors. The mass fractions of acetic and formic acids in the condensates were 0.7 and 0.2 wt%, respectively. Wardell and King [48] report of distribution coefficient of 3.8 or 4.8 for the extraction of 0.5 wt% acetic acid feed with TOPO (21.8 wt%) in a Chevron Solvent 25 diluent, and Golob et al. [49] report of similar distribution coefficients for Chevron 25 and kerosene diluents. It was assumed that undecane, being a constituent in kerosene, and Chevron 25 Solvent behave relatively similarly as diluents. A distribution coefficient of 3 was adopted for acetic acid with a TOPO concentration of 21.8 wt% in undecane. Due to a lower concentration and stronger acidity of formic acid, its distribution coefficient was assumed to be 5. The extraction step was modeled assuming four ideal steps in a mixer-settler type extractor, stage efficiency of 100 %, and slope of the extraction equilibrium line equal to distribution coefficient. TOPO and undecane were assumed immiscible in water in the extraction stage, eliminating the need of a raffinate purification step. TOPO was assumed to extract 1 mol of water per 1 mol of acetic acid [49].

The purification of acetic acid extracted from the evaporator condensates was modeled following the work of Kanzler and Schedler [47]. After extraction, the extract was fed to the first distillation column where an azeotrope of undecane and water was separated as a distillate, condensed, and decanted to separate water and undecane phases. The undecane phase was recycled as a reflux back to the column. The bottom stream from the column was fed to the second column where, in vacuum distillation (5 kPa), part of undecane, the residual water, acetic acid, and formic acid were separated as a distillate, condensed, and decanted. The undecane phase was again recycled as a reflux back to the column. The aqueous phase, containing mainly water, acetic acid, and formic acid, was sent to the third column where acetic acid was produced as a bottom product at a purity of approximately 97 wt%. The distillate, containing formic acid, acetic acid, water, and residual undecane, was decanted to separate undecane and aqueous acid mixture as separate phases. The undecane phase was recycled back to extraction, and the acid mixture was sent to combustion. After a heat exchanger which recovers heat from the bottoms of the first column to the extract stream fed to the first column, the bottoms stream was recycled back to the extraction stage. The number of stages was set to 4, 10, and 50, in the first, second, and third column, respectively. The reflux ratio was set to 6.5 in the third column. No TOPO was assumed to be lost in the process. A flowsheet containing the extraction and distillation of acetic acid stages is presented in ESM Fig. 2S.

### 2.3.5 Enzymatic hydrolysis and fermentation

Reactions, yields, and conditions in separate enzymatic hydrolysis and fermentation stages were set according to the NREL study [36], although the raw materials as well as the pretreatment processes and characteristics of the pretreated materials are relatively different. As in the NREL study [36], the enzyme preparation was assumed to contain hemicellulase activity, enabling a partial conversion of unreacted hemicelluloses to hemicellulosic sugars in the hydrolysis stage. Overall, 82 % of xylan was set to hydrolyze to xylose, as reported in the NREL study [36] for enzymatic hydrolysis using an advanced cellulase preparation with xylanase and xylooligomerase activities. Also other hemicelluloses were set to follow this conversion rate. The conversion rate of cellulose to glucose was 90 %. The temperature, cellulase loading, and residence time in the hydrolysis were 48 °C, 20 mg/g cellulose, and 3.5 days, respectively.

In the model, the total solids contents in hydrolysis and fermentation were approximately 15.5 and 17.9 %, respectively. These differed slightly from the values adopted in the NREL study [36], where total solids content was approximately 20 % in both stages. The differences in solids contents were assumed not to affect the hydrolysis and fermentation yields. Ten percent of combined sugar stream (from enzymatic hydrolysis and the aqueous hemicellulosic sugar stream) was assumed to be fed to an inoculum production train to grow the fermenting organism.

The main parameters used in modeling of the seed train and fermentation stages were adopted from the NREL study [36]. The seed train was a five-stage fermenting system with a batch time of 24 h in each stage. Ninety percent of glucose and 80 % of xylose were converted to ethanol and 4.0 % of both glucose and xylose to *Zymomonas mobilis* (the fermenting organism used in the fermentation stage). Corn steep liquor (0.5 wt%) and diammonium phosphate (0.67 g/L) were used as nutrients in the seed train. The grown inoculum from the fifth stage was then directed to the fermentation stage along with the combined sugar stream. In the fermentation stage, the temperature was 32 °C and residence time 1.5 days. Ninety-five percent of glucose and 85 % of xylose and arabinose were fermented to ethanol. Other hemicellulosic sugars were not assumed to be fermented. Three percent of sugars were lost to side product lactic acid by contaminating microorganisms. Corn steep liquor (0.25 wt%) and diammonium phosphate (0.33 g/L) were used as nutrients in the fermenting stage [36]. A flowsheet containing the enzymatic hydrolysis, seed train, and fermentation stages is presented in ESM Fig. 3S.

### 2.3.6 Ethanol product and solids recovery

Following the NREL study [36], the ethanol product stream purification was assumed to be carried out with two distillation columns and a molecular sieve. The first, a beer column, separated the dissolved $CO_2$ from the fermentation as a distillate and most water and organic residues as a bottoms stream. Most ethanol was recovered as a vapor-side draw and fed to the second column, a rectification column, where ethanol was concentrated to a concentration of approximately 92.5 wt%, before feeding it to the molecular sieve for final purification to a purity of 99.4 wt%. The overhead stream from the beer column was sent to a water scrubber to recover any entrained ethanol back to the process. The bottoms stream from the beer column was fed to a pressure filter to separate insoluble solids. The filter cake was sent to combustion and the filtrate to wastewater treatment (WWT) [36]. A flowsheet containing the ethanol product distillation columns, scrubber, and pressure filter is presented in ESM Fig. 3S.

### 2.3.7 Wastewater treatment

A WWT facility was not explicitly modeled in this study. The amount of biogas and sludge produced in the WWT, and burned in the combustor, was, however, calculated based on the NREL study [36], taking into account different organic loads to the WWT plant.

### 2.3.8 Boiler and turbine and electricity consumption

A boiler, turbine, and steam cycle were modeled in the study. Steam demands of different unit operations of the process were assessed based on the simulation model. Further, preliminary heat integration was carried out for heat recovery and reduction of steam consumption in the process. The recovered heat streams are shown in the process flowsheets (ESM Fig. 1S, 2S, 3S, and 4S). Heat exchanger efficiency was assumed to be 90 %. All feed streams to the process were assumed to be introduced at a temperature of 20 °C.

Bark, biogas and sludge from WWT, and all organic residues separated from the process were burned in the boiler to provide steam and electricity to the process. Depending on the outcome of energy balance calculations, natural gas was assumed to be used as an external energy source to balance the steam and electricity demand, if it was required, and excess electricity was assumed to be sold to the grid, if excess electricity was produced.

The energy formed in the combustion of bark was calculated based on a dry solids lower heating value of bark of 22.5 MJ/kg [50]. The energy of combustion of the other components was calculated based on stoichiometric combustion reactions. On a lower heating value basis, 80 % of total combustion energy was then assumed to be converted to steam heat. The steam side of the boiler and the turbine were modeled following the NREL study [36], with high pressure steam extracted at 1.3 MPa and low pressure steam at 930 kPa, residual steam (if any) condensed at 10 kPa, and isentropic efficiency of the turbine of 85 %.

The electricity consumptions of wood yard, cooking, washing, and screening were estimated based on the work of Fogelholm and Suutela [50]. The electricity consumption of the rest of the process was estimated based on the NREL study [36] and the simulation model. A flowsheet of the boiler and turbine section of the process is presented in ESM Fig. 4S.

### 2.4 Approximate $CO_2$ emissions

Approximate fossil-based $CO_2$ emissions per ethanol energy produced were calculated based on the total natural gas consumption of the process. Natural gas and ethanol were converted to energy basis using lower heating values of 50.0 and 26.8 MJ/kg, respectively. The fossil energy was allocated to the produced ethanol in two different ways. They will be described in subsection 3.2. The allocated natural gas was then converted to $CO_2$ based on a typical total (including upstream processing and combustion) natural gas $CO_2$ emission of 59.2 g/MJ [51].

## 3 Results and discussion

### 3.1 Mass and energy balances

Based on the simulation model, mass and energy balances were compiled for the process. Table 2 presents the main inputs and outputs of the process. Whenever applicable, the flow rates are on a pure component basis. The production rates of ethanol and furfural are net rates, taking into account the make-up ethanol needed in cooking and the furfural used in extraction. A more detailed mass balance is presented in the process flowsheets and stream tables (ESM Fig. 1S, 2S, 3S, 4S, and Table 1S).

**Table 2** The raw materials and products of the process

| | Flow rate, MT/day |
|---|---|
| *Raw materials* | |
| Feedstock (dry) | |
| Hardwood chips | 2,000 |
| Bark and debarking losses | 353 |
| Total feedstock | 2,353 |
| Chemicals, enzyme, and nutrients | |
| $H_2SO_4$ | 20.2 |
| Ammonia | 12.4 |
| Cellulase | 15.5 |
| Corn steep liquor | 25.3 |
| Diammonium phosphate | 3.3 |
| External fuel (natural gas) | |
| To boiler | 45.1 |
| To lignin drying | 10.9 |
| *Products* | |
| Ethanol | 459.1 |
| Organosolv lignin | 310.5 |
| Furfural | 6.6 |
| Acetic acid | 30.3 |
| Excess electricity | 87.0 MWh/day (3.6 MW) |

As can be seen in Table 2, 459.1 MT/d (53.9 million gallons/year) of ethanol was produced from a debarked feedstock flow of 2,000 dry MT/day. Taking into account the assumed carbohydrate content of the raw material (Fig. 2), converted to sugar basis, and the stoichiometric fermentation yield of 51 %, approximately 64 % of carbohydrates were converted to ethanol in this process. This is lower than the 76 % conversion reported in the NREL study [36], which can be attributed to the lower carbohydrate recovery (carbohydrates present in the solid fraction and sugar oligomers and monomers present in the water-soluble fraction over the total amount of carbohydrates in the feedstock) in the organosolv cooking (approximately 84 %) as reported by Pan et al. [10] compared to the NREL dilute acid pretreatment [36] (approximately 98 %). In addition to the differences in experimental setups, raw materials, and assumptions between the organosolv of Pan et al. [10] and the NREL dilute acid study, one possible explanation for the lower carbohydrate yield of the organosolv cooking could be the relatively high temperature and residence time applied in the cooking stage, potentially leading to increased carbohydrate losses.

Approximately 67 % of the original lignin in the wood chips was precipitated and recovered as organosolv lignin (310.5 MT/day) under the conditions applied in the study. Along with ethanol, the production rate of lignin was therefore significant. The production rates of other co-products, furfural (6.6 MT/day), and acetic acid (30.3 MT/day), were significantly lower. Overall, the total yield of recovered products (defined here as the mass of products over the dry mass of debarked feedstock) was approximately 40 %. The corresponding value in the NREL dilute acid study was 26 %, illustrating the relatively high share of the original feedstock being converted to products in the organosolv-based biorefinery.

As can further be seen in Table 2, natural gas (45.1 MT/day, 2300 GJ/day) was needed in the boiler to cover the steam balance. Although concurrently also a small amount of excess electricity (3.6 MW, 310 GJ/day) was produced and sold to the grid, the process was overall not energy self-sufficient with the assumptions adopted in modeling. Pretreatment processes that do not require the recovery of a solvent by distillation and do not aim at the recovery of the lignin fraction typically result in energy self-sufficiency. For example, in the NREL process [36] where there was no need to recover a solvent and the lignin was combusted for energy, a considerable amount of excess electricity (12.8 MW) was produced to the grid without external fuel (or bark) combusted in the boiler. The energy balance of the organosolv process is further analyzed in Table 3 which presents the live steam consumption of the main equipment, total steam consumption of the plant, the fuels burned in the boiler, the steam and electricity production, and the overall electricity consumption. The steam consumption is presented in more detail in the process flowsheets and stream tables (ESM Fig. 1S, 2S, 3S, 4S, and Table 1S), and electricity consumption in a separate table (ESM Table 2S).

As can be seen in Table 3, the live steam consumption of the solvent recovery column I was 3290 GJ/day. Taking into account the consumption of recovered process steam (spent cooking liquor flash steam, see subsection 2.3.2) used in the column, the total heat duty was approximately 5,200 GJ/day. Along with cooking, the solvent recovery was therefore a major steam consumer in the process, increasing the total energy consumption of the process considerably. The increased energy consumption together with the relatively high amount of recovered products resulted in the demand of external fuel. The total energy consumption (calculated here as the difference between the total steam energy produced in the boiler and excess electricity sold to the grid) of the studied organosolv process (approximately 18,100 GJ/day) was approximately 34 % higher than that of the NREL dilute acid process (approximately 13,400 GJ/day). Due to lower carbohydrate to ethanol conversion, the difference in total energy consumption relative to the amount of ethanol produced was even higher, with the organosolv process (approximately 39 GJ/MT ethanol) consuming approximately 49 % more energy than the NREL dilute acid process (approximately 26 GJ/MT ethanol). On the other hand, relative to the total amount of recovered products, the organosolv process consumed a lower amount of energy (approximately 22 GJ/MT products) than the NREL dilute acid process (approximately 26 GJ/MT products).

**Table 3** Steam and electricity consumption and production and feeds to the boiler

| | Duty or flow |
|---|---|
| *Live steam consumption, GJ/day* | |
| Digester | 3,950 |
| Solvent recovery column I | 3,290 |
| EtOH beer column | 2,850 |
| EtOH rectification column | 620 |
| Others | 1,240 |
| Total[a] | 11,950 |
| *Feeds to boiler (on dry basis), MT/day* | |
| Bark | 353 |
| Process residues | 562 |
| Sludge from WWT | 24 |
| Methane from WWT | 85 |
| External natural gas | 45 |
| Total | 1,070 |
| *Boiler feed combustion energy, GJ/day* | |
| Total | 23,000 |
| 80 % to steam energy | 18,400 |
| *Electricity production* | 758 MWh/day<br>(31.6 MW) |
| *Electricity consumption* | 671 MWh/day<br>(27.9 MW) |

[a] The total steam consumption includes only the steam used in indirect heating. Direct steam is used in presteaming of chips before cooking and in steam stripping of furfural

In considering the differences in carbohydrate to ethanol conversion yield and energy consumption discussed in this section between an organosolv and a dilute acid bioethanol production processes, potential trade-off between higher carbohydrate conversion and lower energy consumption of the NREL process and the possibility to recover multiple co-products, especially pure lignin, in the organosolv process, can be seen.

## 3.2 Fossil-based $CO_2$ emissions

The amount of external fossil fuel consumed was used to evaluate the approximate fossil-based $CO_2$ generation of the ethanol produced in the process. The external fossil fuel used in the process, natural gas, was allocated to the produced ethanol in two different ways. First, all the natural gas was allocated to ethanol. Second, the natural gas was apportioned to ethanol (459.1 MT/day, 12,300 GJ/day) and excess electricity (87 MWh/day, 310 GJ/day) produced on an energy content basis. This implies that same overall energy efficiency was assumed for both ethanol and electricity in the calculation. The natural gas apportioned to ethanol was then further allocated to both ethanol and other products produced (furfural, acetic acid, and lignin) on a mass basis (see Table 2). The calculated natural gas consumptions and fossil fuel-based $CO_2$ emissions following these two allocation methods are presented in Table 4.

The US National Renewable Fuel Standard program mandated in the Energy Independence and Security Act of 2007 set a threshold lifecycle greenhouse gas (GHG) reduction for renewable fuels. For cellulosic ethanol, the threshold is currently set at 60 % compared to 2005 gasoline lifecycle GHG emissions [52]. With the baseline

**Table 4** Natural gas consumption and fossil fuel-based $CO_2$ emissions of the ethanol produced in the organosolv process

| Allocation method | MJ of natural gas/MJ of ethanol | g of $CO_2$/MJ of ethanol |
|---|---|---|
| All fossil fuel energy to ethanol | 0.23 | 13.5 |
| Fossil fuel energy to excess electricity on an energy content basis and the rest on mass basis to ethanol and other products | 0.13 | 7.5 |

emissions being 91.3 g of $CO_2$ equivalent/MJ of gasoline [53], the threshold equals to maximum GHG emissions of 36.5 g $CO_2$ equivalent. Although the GHG calculation presented above is not a complete lifecycle analysis on ethanol produced in the organosolv process, it includes the main source of fossil-based emissions for the process, i.e., natural gas. The main element that is excluded is the transportation of the wood, which typically does not add significantly to the overall life cycle GHG emissions [54]. Due to their relatively small amounts, the effect of chemicals, enzyme, and nutrients used in the process on the overall emissions could also be assumed to be rather small. Therefore, the emissions of the organosolv ethanol process can be assumed to be well below the threshold limits, regardless of the way the emissions are allocated to ethanol and other products. Assuming that the lignin product would replace a fossil-based product, it could be given a credit for lowering the consumption of fossil-based raw materials. This would further reduce the overall greenhouse gas emissions of the process. Such analysis was, however, beyond the scope of this study, especially because the end-product application of the lignin product was not specified.

## 4 Conclusions

In the organosolv process, organic solvents are used to dissolve lignin from the lignocellulosic raw material, enabling the production of a pure lignin co-product and a good response to enzymatic hydrolysis. Compared to a more standard dilute acid bioethanol process, the lower carbohydrate recovery in organosolv cooking led, however, to a lower overall carbohydrate to ethanol conversion. In addition, due to the recovery of the solvent, the energy consumption was found to be 34 % higher than in the dilute acid process, and the process was not energy self-sufficient. Although external fuel was needed to cover the steam balance of the process, the fossil-based $CO_2$ emissions were assumed to be well below the US Renewable Fuel Standard threshold limit for cellulosic ethanol.

The recovery of the solvent and co-products increases the number of processing steps and, evidently also, the investment cost. An economic analysis is required to assess whether the production of pure lignin and other co-products is enough to justify the decreased ethanol yield as well as the increased energy consumption and capital expenditures.

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**Biomass Conversion and Biorefinery**

Electronic Supplementary Material for the article:

# Design and simulation of an organosolv process for bioethanol production

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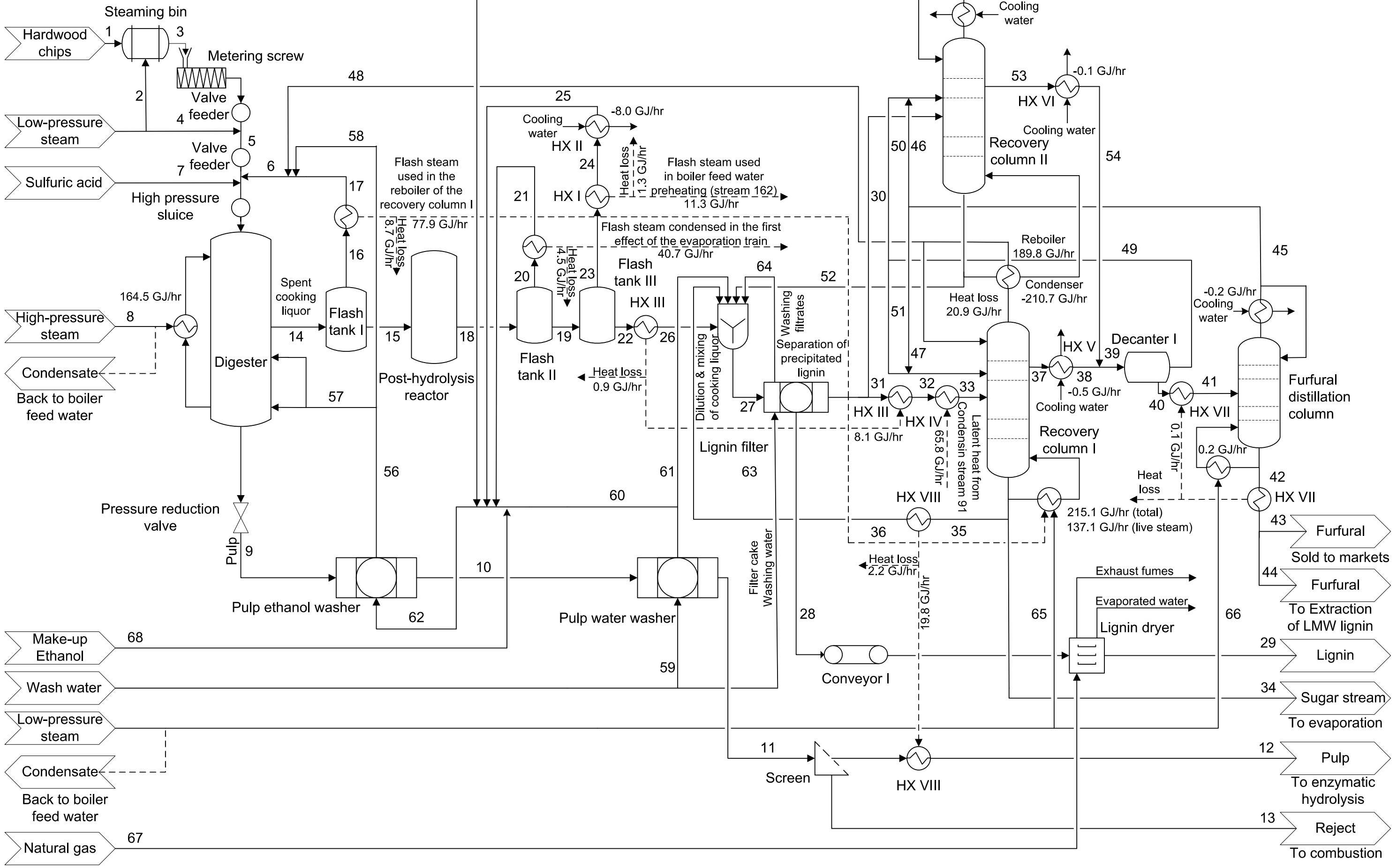
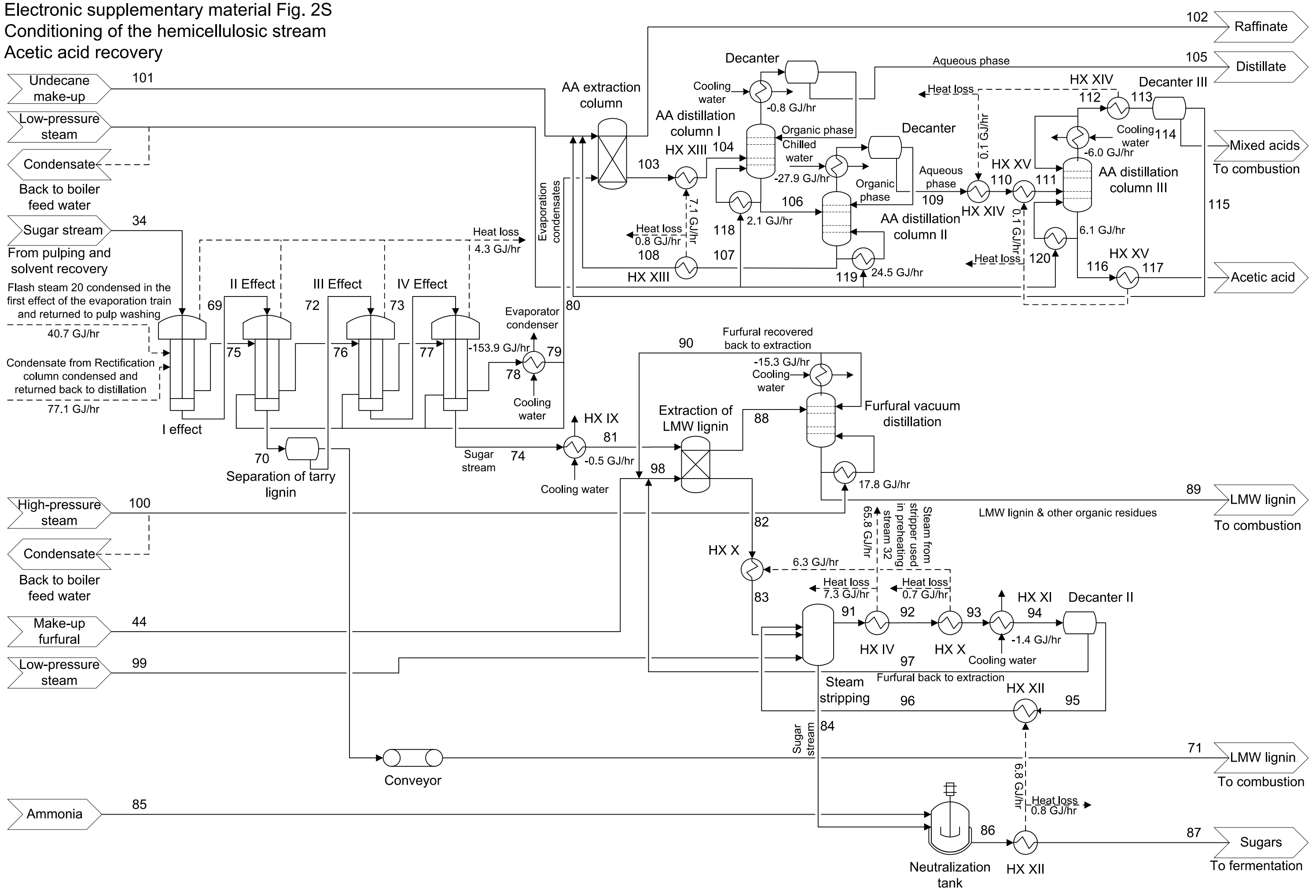
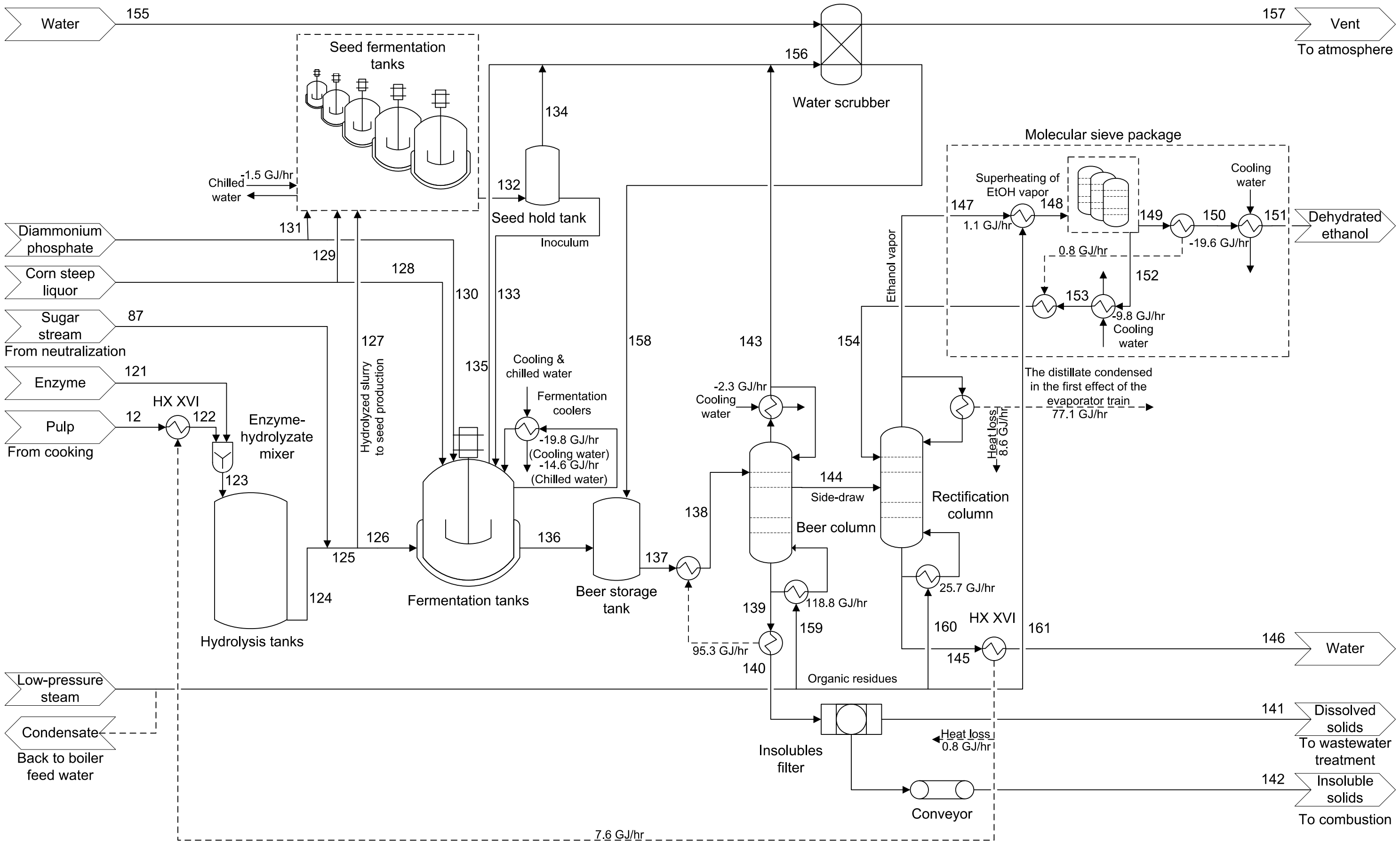
Electronic supplementary material Fig. 1S
Pretreatment and lignin recovery
Solvent and furfural recovery



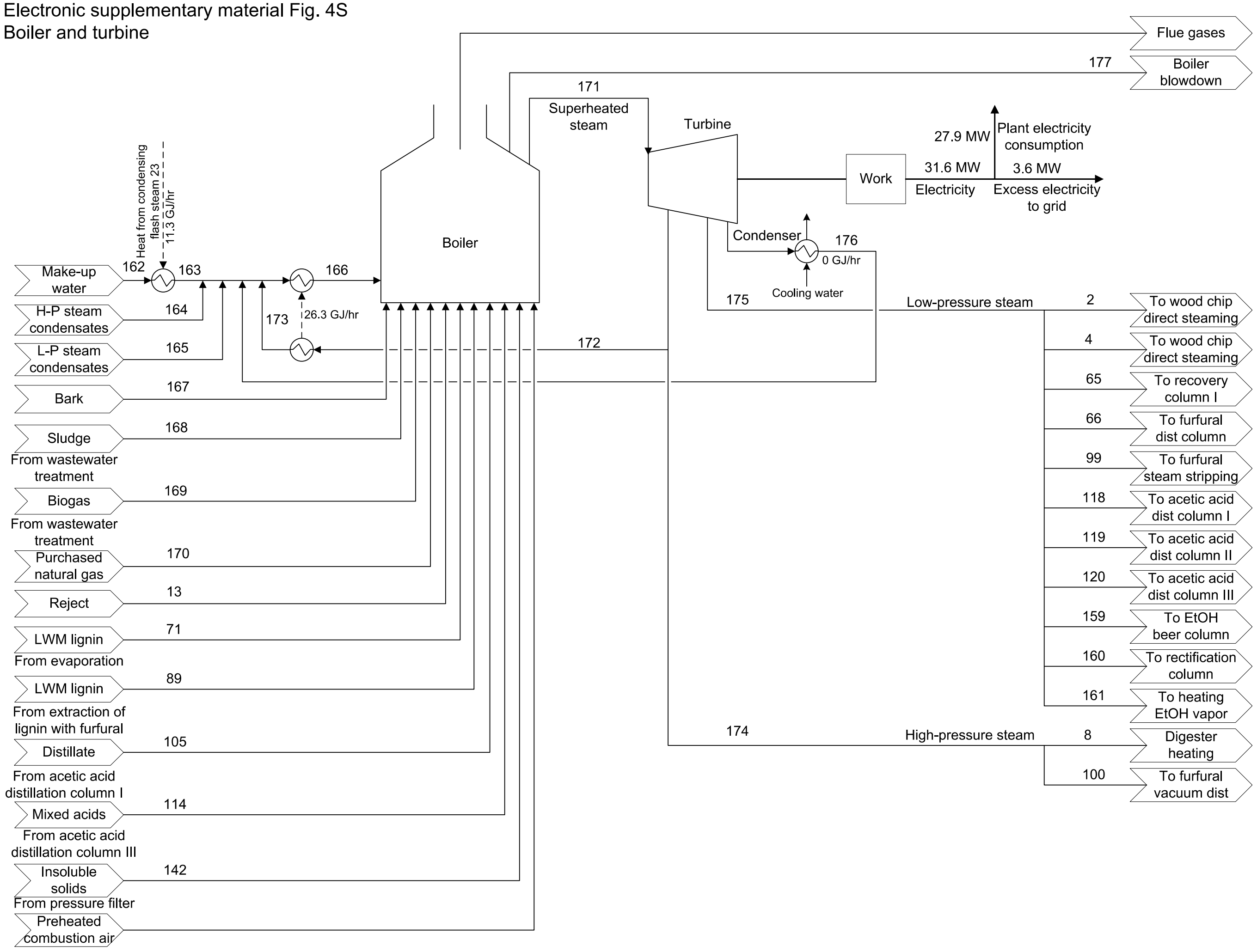
Electronic supplementary material Fig. 2S
Conditioning of the hemicellulosic stream
Acetic acid recovery



Electronic supplementary material Fig. 3S
Enzymatic hydrolysis and fermentation



# Electronic supplementary material Fig. 4S
## Boiler and turbine



## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Total flow | MT/hr | 166.67 | 11.62 | 178.28 | 6.00 | 184.28 | 315.61 | 0.84 | 77.22 | 438.35 | 450.08 | 281.30 | 277.72 | 3.58 | 350.71 | 277.67 | 73.04 | 73.04 | 277.67 | 241.96 | 35.71 |
| Temperature | C | 20 | 240 | 100 | 240 | 130 | 85 | 20 | 273 | 82 | 53 | 20 | 42 | 20 | 180 | 135 | 135 | 128 | 135 | 101 | 101 |
| Pressure | atm | 1.0 | 9.5 | 1.1 | 9.5 | 5.0 | 5.0 | 5.0 | 13.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 19.7 | 5.1 | 5.1 | 5.0 | 5.1 | 1.7 | 1.7 |
| Vapor fraction | | 0.0 | 1.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 1.0 |
| Enthalpy | GJ/hr | -1803.3 | -151.1 | -1954.3 | -78.0 | -2032.4 | -3014.3 | -7.1 | -999.1 | -4468.1 | -4716.5 | -4014.6 | -3948.6 | -46.2 | -3536.6 | -2989.8 | -546.9 | -633.5 | -2982.4 | -2711.5 | -270.9 |
| Glucan | MT/hr | 36.71 | | 36.71 | | 36.71 | | | | 32.37 | 32.37 | 32.37 | 32.37 | | | | | | | | |
| Xylan | MT/hr | 13.09 | | 13.09 | | 13.09 | | | | 2.46 | 2.46 | 2.46 | 2.46 | | | | | | | | |
| Mannan | MT/hr | 2.91 | | 2.91 | | 2.91 | | | | 1.12 | 1.12 | 1.12 | 1.12 | | | | | | | | |
| Galactan | MT/hr | 0.29 | | 0.29 | | 0.29 | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | 0.19 | | 0.19 | | 0.19 | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | 19.38 | | 19.38 | | 19.38 | | | | 5.15 | 5.15 | 5.15 | 5.15 | | | | | | | | |
| Acetate groups | MT/hr | 2.75 | | 2.75 | | 2.75 | | | | 0.52 | 0.52 | 0.52 | 0.52 | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | 1.08 | 1.08 | 1.08 | | 1.08 | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | 8.02 | | 8.02 | | 8.02 | | | | 2.31 | 2.31 | 2.31 | 2.31 | | | | | | | | |
| Water | MT/hr | 83.33 | 11.62 | 94.95 | 6.00 | 100.95 | 121.45 | | 77.22 | 197.47 | 210.05 | 235.90 | 233.40 | 2.50 | 170.92 | 148.53 | 22.39 | 22.39 | 147.98 | 136.83 | 11.15 |
| Ethanol | MT/hr | | | | | | 184.41 | | | 169.41 | 186.31 | 0.37 | 0.37 | 0.00 | 141.92 | 91.46 | 50.46 | 50.46 | 91.46 | 67.02 | 24.43 |
| Glucose | MT/hr | | | | | | 0.03 | | | 0.09 | 0.03 | 0.00 | 0.00 | | 0.13 | 0.13 | | | 0.41 | 0.41 | |
| Other C6 sugars | MT/hr | | | | | | 0.09 | | | 0.26 | 0.08 | 0.00 | 0.00 | 0.00 | 0.37 | 0.37 | | | 1.21 | 1.21 | |
| Xylose | MT/hr | | | | | | 0.77 | | | 2.16 | 0.68 | 0.00 | 0.00 | 0.00 | 3.12 | 3.12 | | | 7.04 | 7.04 | |
| Arabinose | MT/hr | | | | | | 0.04 | | | 0.12 | 0.04 | 0.00 | 0.00 | | 0.17 | 0.17 | | | 0.17 | 0.17 | |
| Sugar oligomers | MT/hr | | | | | | 1.21 | | | 3.39 | 1.06 | 0.00 | 0.00 | 0.00 | 4.89 | 4.89 | | | 0.12 | 0.12 | |
| Lignin (dissolved) | MT/hr | | | | | | 3.87 | | | 10.84 | 3.40 | 0.01 | 0.01 | 0.00 | 15.64 | 15.64 | | | 15.64 | 15.64 | |
| Acetic acid | MT/hr | | | | | | 0.35 | | | 0.79 | 0.38 | 0.00 | 0.00 | 0.00 | 1.05 | 1.00 | 0.05 | 0.05 | 2.13 | 2.08 | 0.05 |
| Formic acid | MT/hr | | | | | | 0.31 | | | 0.69 | 0.33 | 0.00 | 0.00 | 0.00 | 0.90 | 0.86 | 0.04 | 0.04 | 0.87 | 0.85 | 0.02 |
| Furfural | MT/hr | | | | | | 0.33 | | | 0.48 | 0.32 | 0.00 | 0.00 | 0.00 | 0.56 | 0.47 | 0.09 | 0.09 | 0.54 | 0.49 | 0.05 |
| Levulinic acid | MT/hr | | | | | | 0.52 | | | 1.43 | 0.45 | 0.00 | 0.00 | 0.00 | 2.07 | 2.06 | 0.00 | 0.00 | 2.08 | 2.08 | 0.00 |
| 5-HMF | MT/hr | | | | | | 0.02 | | | 0.05 | 0.02 | 0.00 | 0.00 | | 0.08 | 0.08 | | | 0.10 | 0.10 | |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | | | | | | 1.84 | | | 5.14 | 1.62 | 0.00 | 0.00 | 0.00 | 7.42 | 7.42 | | | 6.44 | 6.44 | |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | | | | | | 0.20 | 0.84 | | 0.56 | 0.17 | 0.00 | 0.00 | 0.00 | 0.80 | 0.80 | 0.00 | 0.00 | 0.80 | 0.80 | 0.00 |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | | | | | 0.17 | | | 0.47 | 0.15 | 0.00 | 0.00 | 0.00 | 0.68 | 0.68 | | | 0.68 | 0.68 | |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | | | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Total flow | MT/hr | 35.71 | 226.29 | 15.67 | 15.67 | 15.67 | 226.29 | 828.57 | 18.48 | 13.09 | 372.96 | 437.12 | 437.12 | 437.12 | 296.52 | 79.06 | 79.06 | 2.99 | 2.99 | 5.47 | 0.57 |
| Temperature | C | 94 | 77 | 77 | 72 | 71 | 62 | 50 | 22 | 22 | 50 | 50 | 55 | 93 | 100 | 100 | 30 | 90 | 40 | 40 | 40 |
| Pressure | atm | 1.7 | 0.7 | 0.7 | 0.7 | 0.7 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Vapor fraction | | 0.0 | 0.0 | 1.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Enthalpy | GJ/hr | -316.1 | -2592.0 | -119.6 | -132.1 | -140.1 | -2600.9 | -11293.1 | -170.2 | -85.0 | -5146.5 | -6031.8 | -6023.8 | -5958.0 | -4362.6 | -1163.2 | -1185.2 | -33.0 | -33.5 | -61.9 | -2.2 |
| Glucan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | | | | | | | 12.94 | 12.94 | | | | | | | | | | | |
| Acetate groups | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Water | MT/hr | 11.15 | 131.91 | 4.92 | 4.92 | 4.92 | 131.91 | 651.10 | 5.48 | 0.13 | 297.73 | 348.95 | 348.95 | 348.95 | 269.92 | 71.97 | 71.97 | 1.84 | 1.84 | 3.44 | 0.06 |
| Ethanol | MT/hr | 24.43 | 56.33 | 10.70 | 10.70 | 10.70 | 56.33 | 101.19 | 0.04 | | 46.27 | 54.23 | 54.23 | 54.23 | 0.00 | 0.00 | 0.00 | 0.43 | 0.43 | 0.66 | 0.04 |
| Glucose | MT/hr | | 0.41 | | | | 0.41 | 0.99 | 0.00 | 0.00 | 0.45 | 0.53 | 0.53 | 0.53 | 0.42 | 0.11 | 0.11 | | | | |
| Other C6 sugars | MT/hr | | 1.21 | | | | 1.21 | 2.91 | 0.00 | 0.00 | 1.33 | 1.56 | 1.56 | 1.56 | 1.23 | 0.33 | 0.33 | | | | |
| Xylose | MT/hr | | 7.04 | | | | 7.04 | 17.00 | 0.01 | 0.01 | 7.77 | 9.11 | 9.11 | 9.11 | 7.19 | 1.92 | 1.92 | | | | |
| Arabinose | MT/hr | | 0.17 | | | | 0.17 | 0.41 | 0.00 | 0.00 | 0.19 | 0.22 | 0.22 | 0.22 | 0.18 | 0.05 | 0.05 | | | | |
| Sugar oligomers | MT/hr | | 0.12 | | | | 0.12 | 0.87 | 0.00 | 0.00 | 0.40 | 0.47 | 0.47 | 0.47 | 0.37 | 0.10 | 0.10 | | | | |
| Lignin (dissolved) | MT/hr | | 15.64 | | | | 15.64 | 21.24 | 0.00 | 0.00 | 3.80 | 4.45 | 4.45 | 4.45 | 3.51 | 0.94 | 0.94 | | | | |
| Acetic acid | MT/hr | 0.05 | 2.06 | 0.02 | 0.02 | 0.02 | 2.06 | 5.05 | 0.00 | 0.00 | 2.31 | 2.70 | 2.70 | 2.70 | 2.14 | 0.57 | 0.57 | 0.06 | 0.06 | 0.13 | 0.01 |
| Formic acid | MT/hr | 0.02 | 0.84 | 0.01 | 0.01 | 0.01 | 0.84 | 2.05 | 0.00 | | 0.94 | 1.10 | 1.10 | 1.10 | 0.87 | 0.23 | 0.23 | 0.01 | 0.01 | 0.03 | 0.00 |
| Furfural | MT/hr | 0.05 | 0.46 | 0.02 | 0.02 | 0.02 | 0.46 | 0.55 | 0.00 | 0.00 | 0.25 | 0.30 | 0.30 | 0.30 | 0.02 | 0.01 | 0.01 | 0.64 | 0.64 | 1.22 | 0.45 |
| Levulinic acid | MT/hr | 0.00 | 2.08 | 0.00 | 0.00 | 0.00 | 2.08 | 5.17 | 0.00 | 0.00 | 2.36 | 2.77 | 2.77 | 2.77 | 2.19 | 0.58 | 0.58 | | | | |
| 5-HMF | MT/hr | | 0.10 | | | | 0.10 | 0.25 | 0.00 | 0.00 | 0.12 | 0.14 | 0.14 | 0.14 | 0.11 | 0.03 | 0.03 | | | | |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | | 6.44 | | | | 6.44 | 16.11 | 0.01 | 0.01 | 7.37 | 8.63 | 8.63 | 8.63 | 6.82 | 1.82 | 1.82 | | | | |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | 0.00 | 0.80 | | | | 0.80 | 1.99 | 0.00 | 0.00 | 0.91 | 1.07 | 1.07 | 1.07 | 0.84 | 0.22 | 0.22 | | | | |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | 0.68 | | | | 0.68 | 1.68 | 0.00 | 0.00 | 0.77 | 0.90 | 0.90 | 0.90 | 0.71 | 0.19 | 0.19 | | | | |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | | | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |
| Total flow | MT/hr | 0.57 | 0.44 | 0.28 | 0.16 | 0.12 | 0.06 | 0.07 | 61.27 | 4.90 | 2.26 | 2.65 | 320.47 | 2.48 | 2.48 | 52.33 | 469.63 | 288.32 | 181.30 | 326.14 | 377.23 |
| Temperature | C | 105 | 156 | 50 | 50 | 85 | 85 | 85 | 78 | 40 | 40 | 40 | 58 | 51 | 40 | 40 | 73 | 73 | 73 | 20 | 46 |
| Pressure | atm | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.2 | 0.2 | 1.0 | 0.2 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Vapor fraction | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Enthalpy | GJ/hr | -2.1 | -0.8 | -0.6 | -0.3 | -1.2 | -0.6 | -0.7 | -427.6 | -59.7 | -27.5 | -32.2 | -4770.7 | -28.2 | -28.3 | -370.5 | -5059.9 | -3106.5 | -1953.4 | -5174.6 | -4479.1 |
| Glucan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Acetate groups | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Water | MT/hr | 0.06 | 0.00 | 0.00 | 0.00 | 0.06 | 0.03 | 0.03 | 7.07 | 3.38 | 1.56 | 1.82 | 291.81 | 1.59 | 1.59 | 5.91 | 238.28 | 146.29 | 91.99 | 326.14 | 228.88 |
| Ethanol | MT/hr | 0.04 | 0.00 | 0.00 | 0.00 | 0.04 | 0.02 | 0.02 | 54.15 | 0.62 | 0.28 | 0.33 | 0.00 | 0.22 | 0.22 | 46.35 | 206.72 | 126.91 | 79.81 | | 141.72 |
| Glucose | MT/hr | | | | | | | | | | | | 0.45 | | | | 0.08 | 0.05 | 0.03 | | 0.02 |
| Other C6 sugars | MT/hr | | | | | | | | | | | | 1.33 | | | | 0.24 | 0.15 | 0.09 | | 0.06 |
| Xylose | MT/hr | | | | | | | | | | | | 7.77 | | | | 2.00 | 1.23 | 0.77 | | 0.52 |
| Arabinose | MT/hr | | | | | | | | | | | | 0.19 | | | | 0.11 | 0.07 | 0.04 | | 0.03 |
| Sugar oligomers | MT/hr | | | | | | | | | | | | 0.40 | | | | 3.13 | 1.92 | 1.21 | | 0.81 |
| Lignin (dissolved) | MT/hr | | | | | | | | | | | | 3.80 | | | | 10.02 | 6.15 | 3.87 | | 2.59 |
| Acetic acid | MT/hr | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.11 | 0.05 | 0.06 | 2.30 | 0.06 | 0.06 | 0.00 | 0.78 | 0.48 | 0.30 | | 0.29 |
| Formic acid | MT/hr | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.03 | 0.02 | 0.02 | 0.89 | 0.02 | 0.02 | 0.04 | 0.68 | 0.42 | 0.26 | | 0.25 |
| Furfural | MT/hr | 0.45 | 0.44 | 0.28 | 0.16 | 0.01 | 0.01 | 0.01 | 0.05 | 0.76 | 0.35 | 0.41 | 0.00 | 0.58 | 0.58 | 0.03 | 0.51 | 0.31 | 0.20 | | 0.24 |
| Levulinic acid | MT/hr | | | | | | | | | | | | 2.36 | | | | 1.33 | 0.81 | 0.51 | | 0.34 |
| 5-HMF | MT/hr | | | | | | | | | | | | 0.12 | | | | 0.05 | 0.03 | 0.02 | | 0.01 |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | | | | | | | | | | | | 7.37 | | | | 4.76 | 2.92 | 1.84 | | 1.23 |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | | | | | | | | | | | | 0.91 | | | | 0.51 | 0.32 | 0.20 | | 0.13 |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | | | | | | | | | | | 0.77 | | | | 0.43 | 0.27 | 0.17 | | 0.11 |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | | | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

|  | Unit |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream |  | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| Total flow | MT/hr | 117.69 | 481.36 | 85.06 | 85.06 | 63.97 | 0.11 | 0.45 | 0.42 | 235.67 | 172.64 | 3.01 | 169.63 | 105.16 | 39.71 | 60.85 | 63.03 | 64.48 | 65.44 | 65.44 | 253.79 |
| Temperature | C | 46 | 49 | 20 | 22 | 240 | 240 | 25 | 20 | 87 | 77 | 77 | 77 | 66 | 48 | 87 | 77 | 66 | 48 | 48 | 69 |
| Pressure | atm | 1.0 | 1.0 | 1.0 | 1.0 | 9.5 | 9.5 | 1.0 | 1.0 | 0.6 | 0.4 | 1.0 | 0.4 | 0.2 | 0.1 | 0.6 | 0.4 | 0.2 | 0.1 | 0.1 | 1.0 |
| Vapor fraction |  | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 0.0 |
| Enthalpy | GJ/hr | -1397.4 | -5308.3 | -1349.6 | -1338.8 | -831.8 | -1.5 | -2.1 | -2.5 | -3437.4 | -2463.4 | -19.2 | -2444.3 | -1443.9 | -425.7 | -807.4 | -837.2 | -857.2 | -870.1 | -1024.0 | -3958.3 |
| Glucan | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Xylan | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mannan | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Galactan | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Arabinan | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Lignin (insoluble) | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Acetate groups | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Rejects | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Enzyme | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Cell mass | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| TOPO | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Other insolub. solids | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Water | MT/hr | 71.41 | 250.86 | 85.06 | 84.01 | 63.97 | 0.11 |  |  | 209.48 | 146.91 | 0.78 | 146.12 | 82.21 | 17.66 | 60.44 | 62.57 | 63.91 | 64.55 | 64.55 | 251.48 |
| Ethanol | MT/hr | 44.21 | 223.62 |  | 0.65 |  |  |  | 0.42 | 0.00 | 0.00 |  | 0.00 | 0.00 |  | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Glucose | MT/hr | 0.01 | 0.02 |  | 0.01 |  |  |  |  | 0.42 | 0.42 | 0.00 | 0.42 | 0.42 | 0.42 |  |  |  |  |  |  |
| Other C6 sugars | MT/hr | 0.02 | 0.06 |  | 0.02 |  |  |  |  | 1.23 | 1.23 | 0.01 | 1.23 | 1.23 | 1.23 |  |  |  |  |  |  |
| Xylose | MT/hr | 0.16 | 0.52 |  | 0.11 |  |  |  |  | 7.19 | 7.19 | 0.04 | 7.15 | 7.15 | 7.15 |  |  |  |  |  |  |
| Arabinose | MT/hr | 0.01 | 0.03 |  | 0.00 |  |  |  |  | 0.18 | 0.18 | 0.00 | 0.17 | 0.17 | 0.17 |  |  |  |  |  |  |
| Sugar oligomers | MT/hr | 0.25 | 0.81 |  | 0.01 |  |  |  |  | 0.37 | 0.37 | 0.00 | 0.37 | 0.37 | 0.37 |  |  |  |  |  |  |
| Lignin (dissolved) | MT/hr | 0.81 | 2.59 |  | 0.05 |  |  |  |  | 3.51 | 3.51 | 2.11 | 1.40 | 1.40 | 1.40 |  |  |  |  |  |  |
| Acetic acid | MT/hr | 0.09 | 0.36 |  | 0.03 |  |  |  |  | 1.84 | 1.49 | 0.01 | 1.48 | 1.06 | 0.44 | 0.30 | 0.35 | 0.43 | 0.61 | 0.61 | 1.69 |
| Formic acid | MT/hr | 0.08 | 0.32 |  | 0.01 |  |  |  |  | 0.79 | 0.69 | 0.00 | 0.69 | 0.55 | 0.29 | 0.08 | 0.10 | 0.13 | 0.27 | 0.27 | 0.57 |
| Furfural | MT/hr | 0.08 | 0.35 |  | 0.00 |  |  |  |  | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 |
| Levulinic acid | MT/hr | 0.11 | 0.34 |  | 0.03 |  |  |  |  | 2.18 | 2.18 | 0.01 | 2.17 | 2.16 | 2.15 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.02 |
| 5-HMF | MT/hr | 0.00 | 0.01 |  | 0.00 |  |  |  |  | 0.11 | 0.11 | 0.00 | 0.11 | 0.11 | 0.11 |  |  |  |  |  |  |
| Undecane | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Other org. dissolved solids | MT/hr | 0.38 | 1.23 |  | 0.10 |  |  |  |  | 6.82 | 6.82 | 0.04 | 6.78 | 6.78 | 6.78 |  |  |  |  |  |  |
| Other organics | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Sulfuric acid | MT/hr | 0.04 | 0.13 |  | 0.01 |  |  |  |  | 0.84 | 0.84 | 0.00 | 0.84 | 0.84 | 0.84 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ammonia | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Other inorg. dissolved soli | MT/hr | 0.04 | 0.11 |  | 0.01 |  |  |  |  | 0.71 | 0.71 | 0.00 | 0.71 | 0.71 | 0.71 |  |  |  |  |  |  |
| Carbon dioxide | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Methane | MT/hr |  |  |  |  |  |  | 0.45 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| O2 | MT/hr |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

# Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 |
| Total flow | MT/hr | 39.71 | 38.28 | 38.28 | 62.24 | 0.52 | 62.75 | 62.75 | 20.12 | 7.34 | 12.78 | 40.50 | 40.50 | 40.50 | 40.50 | 34.76 | 34.76 | 5.74 | 18.69 | 29.70 | 8.36 |
| Temperature | C | 40 | 40 | 93 | 101 | 20 | 101 | 70 | 40 | 184 | 40 | 99 | 98 | 50 | 40 | 40 | 91 | 40 | 40 | 240 | 273 |
| Pressure | atm | 1.0 | 1.0 | 1.0 | 1.0 | 9.0 | 5.0 | 1.0 | 1.0 | 0.1 | 0.1 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 9.5 | 13.0 |
| Vapor fraction | | 0.0 | 0.0 | 0.0 | 0.0 | 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 | 0.0 | 1.0 | 1.0 |
| Enthalpy | GJ/hr | -426.2 | -400.6 | -394.3 | -837.0 | -2.0 | -840.8 | -848.3 | -132.6 | -42.0 | -88.1 | -426.1 | -499.2 | -506.2 | -507.6 | -489.4 | -482.6 | -18.2 | -106.9 | -386.2 | -108.2 |
| Glucan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Acetate groups | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Water | MT/hr | 17.66 | 18.08 | 18.08 | 47.36 | | 47.36 | 47.36 | 4.28 | 0.00 | 4.28 | 30.36 | 30.36 | 30.36 | 30.36 | 29.93 | 29.93 | 0.42 | 4.71 | 29.70 | 8.36 |
| Ethanol | MT/hr | | 0.00 | 0.00 | | | | | 0.00 | | 0.00 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.00 | 0.00 | | |
| Glucose | MT/hr | 0.42 | 0.37 | 0.37 | 0.37 | | 0.37 | 0.37 | 0.04 | 0.04 | | | | | | | | | | | |
| Other C6 sugars | MT/hr | 1.23 | 1.10 | 1.10 | 1.10 | | 1.10 | 1.10 | 0.12 | 0.12 | | | | | | | | | | | |
| Xylose | MT/hr | 7.15 | 6.44 | 6.44 | 6.44 | | 6.44 | 6.44 | 0.72 | 0.72 | | | | | | | | | | | |
| Arabinose | MT/hr | 0.17 | 0.16 | 0.16 | 0.16 | | 0.16 | 0.16 | 0.02 | 0.02 | | | | | | | | | | | |
| Sugar oligomers | MT/hr | 0.37 | 0.33 | 0.33 | 0.33 | | 0.33 | 0.33 | 0.04 | 0.04 | | | | | | | | | | | |
| Lignin (dissolved) | MT/hr | 1.40 | 0.16 | 0.16 | 0.16 | | 0.16 | 0.16 | 1.25 | 1.25 | | | | | | | | | | | |
| Acetic acid | MT/hr | 0.44 | 0.56 | 0.56 | 0.44 | | | | 0.40 | 0.00 | 0.40 | 0.96 | 0.96 | 0.96 | 0.96 | 0.84 | 0.84 | 0.12 | 0.52 | | |
| Formic acid | MT/hr | 0.29 | 0.30 | 0.30 | 0.29 | | | | 0.12 | 0.00 | 0.12 | 0.38 | 0.38 | 0.38 | 0.38 | 0.37 | 0.37 | 0.01 | 0.14 | | |
| Furfural | MT/hr | 0.00 | 5.27 | 5.27 | 0.09 | | 0.09 | 0.09 | 8.05 | 0.08 | 7.97 | 8.77 | 8.77 | 8.77 | 8.77 | 3.59 | 3.59 | 5.18 | 13.32 | | |
| Levulinic acid | MT/hr | 2.15 | 0.78 | 0.78 | 0.78 | | | | 1.38 | 1.38 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | |
| 5-HMF | MT/hr | 0.11 | 0.04 | 0.04 | 0.04 | | 0.04 | 0.04 | 0.06 | 0.06 | | | | | | | | | | | |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | 6.78 | 3.76 | 3.76 | 3.76 | | 5.61 | 5.61 | 3.01 | 3.01 | | | | | | | | | | | |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | 0.84 | 0.49 | 0.49 | 0.49 | | | | 0.35 | 0.35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.00 | | |
| Ammonia | MT/hr | | | | | 0.52 | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | 0.71 | 0.43 | 0.43 | 0.43 | | 1.09 | 1.09 | 0.28 | 0.28 | | | | | | | | | | | |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | | | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 | 120 |
| Total flow | MT/hr | 0.00 | 251.17 | 129.63 | 129.63 | 0.40 | 129.23 | 126.91 | 126.91 | 2.32 | 2.32 | 2.32 | 1.02 | 1.02 | 0.93 | 0.08 | 1.30 | 1.30 | 0.96 | 11.44 | 2.83 |
| Temperature | C | 20 | 70 | 70 | 92 | 85 | 101 | 101 | 73 | 27 | 56 | 84 | 100 | 37 | 37 | 37 | 118 | 60 | 240 | 240 | 240 |
| Pressure | atm | 1.0 | 1.0 | 1.0 | 1.5 | 1.0 | 1.0 | 0.0 | 1.0 | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 9.5 | 9.5 | 9.5 |
| Vapor fraction | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 |
| Enthalpy | GJ/hr | 0.0 | -3933.7 | -220.4 | -213.3 | -5.4 | -206.6 | -187.6 | -195.5 | -19.0 | -19.8 | -19.7 | -9.5 | -9.6 | -9.0 | -0.2 | -10.1 | -10.2 | -12.5 | -148.8 | -36.8 |
| Glucan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Acetate groups | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | 27.67 | 27.67 | | 27.67 | 27.67 | 27.67 | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Water | MT/hr | | 251.01 | 0.47 | 0.47 | 0.29 | 0.18 | | | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.00 | 0.00 | 0.00 | 0.96 | 11.44 | 2.83 |
| Ethanol | MT/hr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | |
| Glucose | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other C6 sugars | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Xylose | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinose | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sugar oligomers | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (dissolved) | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Acetic acid | MT/hr | | 0.13 | 1.63 | 1.63 | 0.01 | 1.62 | 0.06 | 0.06 | 1.56 | 1.56 | 1.56 | 0.29 | 0.29 | 0.29 | 0.00 | 1.26 | 1.26 | | | |
| Formic acid | MT/hr | | 0.01 | 0.57 | 0.57 | 0.10 | 0.46 | | | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 | 0.00 | 0.00 | 0.00 | | | |
| Furfural | MT/hr | | 0.01 | 0.02 | 0.02 | 0.00 | 0.02 | | | 0.02 | 0.02 | 0.02 | | | | | 0.02 | 0.02 | | | |
| Levulinic acid | MT/hr | | 0.01 | 0.04 | 0.04 | 0.00 | 0.04 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | | | | | 0.02 | 0.02 | | | |
| 5-HMF | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Undecane | MT/hr | 0.00 | | 99.24 | 99.24 | 0.00 | 99.24 | 99.16 | 99.16 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.00 | 0.08 | 0.00 | 0.00 | | | |
| Other org. dissolved solids | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | | 0.00 | | | | | | | | | | | | | | | | | | |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | | | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 121 | 122 | 123 | 124 | 125 | 126 | 127 | 128 | 129 | 130 | 131 | 132 | 133 | 134 | 135 | 136 | 137 | 138 | 139 | 140 |
| Total flow | MT/hr | 11.56 | 277.72 | 289.28 | 289.28 | 352.03 | 316.83 | 35.20 | 0.88 | 0.18 | 0.12 | 0.02 | 35.40 | 33.61 | 1.79 | 16.66 | 334.77 | 352.82 | 352.82 | 301.54 | 301.54 |
| Temperature | C | 20 | 49 | 48 | 48 | 52 | 52 | 52 | 20 | 20 | 20 | 20 | 32 | 32 | 32 | 32 | 32 | 32 | 101 | 125 | 47 |
| Pressure | atm | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 6.0 | 2.3 | 6.3 |
| Vapor fraction | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Enthalpy | GJ/hr | -175.2 | -3941.0 | -4116.2 | -4114.9 | -4963.2 | -4466.9 | -496.3 | -9.3 | -1.9 | -1.0 | -0.2 | -502.2 | -486.3 | -15.9 | -148.1 | -4849.9 | -5131.2 | -5036.0 | -4406.5 | -4502.5 |
| Glucan | MT/hr | | 32.37 | 32.37 | 1.55 | 1.55 | 1.40 | 0.16 | | | | | 0.16 | 0.16 | | | 1.55 | 1.55 | 1.55 | 1.55 | 1.55 |
| Xylan | MT/hr | | 2.46 | 2.46 | 0.44 | 0.44 | 0.40 | 0.04 | | | | | 0.04 | 0.04 | | | 0.44 | 0.44 | 0.44 | 0.44 | 0.44 |
| Mannan | MT/hr | | 1.12 | 1.12 | 0.20 | 0.20 | 0.18 | 0.02 | | | | | 0.02 | 0.02 | | | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | 5.15 | 5.15 | 5.15 | 5.15 | 4.64 | 0.52 | | | | | 0.52 | 0.52 | | | 5.15 | 5.15 | 5.15 | 5.15 | 5.15 |
| Acetate groups | MT/hr | | 0.52 | 0.52 | 0.52 | 0.52 | 0.47 | 0.05 | | | | | 0.05 | 0.05 | | | 0.52 | 0.52 | 0.52 | 0.52 | 0.52 |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | 0.65 | | 0.65 | 0.65 | 0.65 | 0.58 | 0.06 | | | | | 0.06 | 0.06 | | | 0.65 | 0.65 | 0.65 | 0.65 | 0.65 |
| Cell mass | MT/hr | | | | | | | | | | | | 0.14 | 0.14 | | | 0.73 | 0.73 | 0.73 | 0.73 | 0.73 |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | 2.31 | 2.31 | 2.31 | 2.31 | 2.08 | 0.23 | 0.22 | 0.04 | | | 0.27 | 0.27 | | | 2.53 | 2.53 | 2.53 | 2.53 | 2.53 |
| Water | MT/hr | 10.91 | 233.40 | 244.31 | 240.68 | 288.03 | 259.23 | 28.80 | 0.44 | 0.09 | | | 28.92 | 28.89 | 0.03 | 0.32 | 288.34 | 305.96 | 305.96 | 274.99 | 274.99 |
| Ethanol | MT/hr | | 0.37 | 0.37 | 0.37 | 0.37 | 0.33 | 0.04 | | | | | 1.91 | 1.88 | 0.03 | 0.30 | 19.29 | 19.70 | 19.70 | 0.07 | 0.07 |
| Glucose | MT/hr | | 0.00 | 0.00 | 32.37 | 32.75 | 29.47 | 3.27 | | | | | 0.16 | 0.16 | | | 0.57 | 0.57 | 0.57 | 0.57 | 0.57 |
| Other C6 sugars | MT/hr | | 0.00 | 0.00 | 1.43 | 2.53 | 2.28 | 0.25 | | | | | 0.25 | 0.25 | | | 2.47 | 2.47 | 2.47 | 2.47 | 2.47 |
| Xylose | MT/hr | | 0.00 | 0.00 | 2.30 | 8.74 | 7.86 | 0.87 | | | | | 0.09 | 0.09 | | | 0.56 | 0.56 | 0.56 | 0.56 | 0.56 |
| Arabinose | MT/hr | | 0.00 | 0.00 | 0.00 | 0.16 | 0.14 | 0.02 | | | | | 0.00 | 0.00 | | | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Sugar oligomers | MT/hr | | 0.00 | 0.00 | 1.30 | 1.63 | 1.46 | 0.16 | | | | | 0.16 | 0.16 | | | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 |
| Lignin (dissolved) | MT/hr | | 0.01 | 0.01 | 0.01 | 0.16 | 0.15 | 0.02 | | | | | 0.02 | 0.02 | | | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 |
| Acetic acid | MT/hr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Formic acid | MT/hr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Furfural | MT/hr | | 0.00 | 0.00 | 0.00 | 0.09 | 0.08 | 0.01 | | | | | 0.01 | 0.01 | 0.00 | 0.00 | 0.09 | 0.09 | 0.09 | 0.04 | 0.04 |
| Levulinic acid | MT/hr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.00 | 0.00 | | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5-HMF | MT/hr | | 0.00 | 0.00 | 0.00 | 0.04 | 0.04 | 0.00 | | | | | 0.00 | 0.00 | | | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | | 0.00 | 0.00 | 0.00 | 5.62 | 5.06 | 0.56 | 0.22 | 0.04 | | | 0.61 | 0.61 | | | 7.08 | 7.08 | 7.08 | 7.07 | 7.07 |
| Other organics | MT/hr | | | | | | | | | | | | 0.09 | 0.09 | | | 0.92 | 0.92 | 0.92 | 0.92 | 0.92 |
| Sulfuric acid | MT/hr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.00 | 0.00 | | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | 0.00 | 0.00 | 0.00 | 1.09 | 0.98 | 0.11 | | | 0.12 | 0.02 | 0.13 | 0.13 | | | 1.22 | 1.22 | 1.22 | 1.22 | 1.22 |
| Carbon dioxide | MT/hr | | | | | | | | | | | | 1.77 | 0.06 | 1.71 | 15.93 | 0.61 | 0.64 | 0.64 | 0.00 | 0.00 |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | 0.01 | 0.00 | 0.01 | 0.11 | 0.00 | 0.00 | 0.00 | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 141 | 142 | 143 | 144 | 145 | 146 | 147 | 148 | 149 | 150 | 151 | 152 | 153 | 154 | 155 | 156 | 157 | 158 | 159 | 160 |
| Total flow | MT/hr | 283.25 | 18.29 | 0.72 | 50.56 | 30.89 | 30.89 | 26.42 | 26.42 | 19.67 | 19.67 | 19.67 | 6.75 | 6.75 | 6.75 | 17.48 | 19.17 | 18.60 | 18.05 | 55.37 | 11.99 |
| Temperature | C | 47 | 47 | 60 | 116 | 121 | 58 | 92 | 116 | 116 | 92 | 38 | 116 | 35 | 71 | 20 | 33 | 24 | 32 | 240 | 240 |
| Pressure | atm | 6.3 | 6.3 | 2.0 | 2.1 | 2.0 | 1.0 | 1.7 | 1.7 | 1.7 | 1.4 | 1.0 | 1.7 | 2.5 | 1.7 | 5.0 | 1.0 | 0.9 | 0.9 | 9.5 | 9.5 |
| Vapor fraction | | 0.0 | 0.0 | 1.0 | 1.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 0.0 | 1.0 | 1.0 |
| Enthalpy | GJ/hr | -4333.9 | -168.7 | -6.2 | -506.9 | -476.3 | -484.8 | -148.2 | -147.2 | -98.3 | -99.1 | -118.7 | -48.8 | -58.6 | -57.8 | -277.6 | -170.2 | -166.3 | -281.3 | -720.0 | -156.0 |
| Glucan | MT/hr | 0.03 | 1.52 | | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | 0.01 | 0.43 | | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | 0.00 | 0.20 | | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | 0.10 | 5.05 | | | | | | | | | | | | | | | | | | |
| Acetate groups | MT/hr | 0.01 | 0.51 | | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | 0.01 | 0.63 | | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | 0.01 | 0.72 | | | | | | | | | | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | 0.05 | 2.48 | | | | | | | | | | | | | | | | | | |
| Water | MT/hr | 268.59 | 6.40 | 0.03 | 30.94 | 30.84 | 30.84 | 1.96 | 1.96 | 0.10 | 0.10 | 0.10 | 1.86 | 1.86 | 1.86 | 17.48 | 0.38 | 0.25 | 17.62 | 55.37 | 11.99 |
| Ethanol | MT/hr | 0.07 | 0.00 | 0.08 | 19.55 | 0.00 | 0.00 | 24.43 | 24.43 | 19.55 | 19.55 | 19.55 | 4.89 | 4.89 | 4.89 | | 0.41 | 0.00 | 0.41 | | |
| Glucose | MT/hr | 0.56 | 0.01 | | | | | | | | | | | | | | | | | | |
| Other C6 sugars | MT/hr | 2.41 | 0.06 | | | | | | | | | | | | | | | | | | |
| Xylose | MT/hr | 0.55 | 0.01 | | | | | | | | | | | | | | | | | | |
| Arabinose | MT/hr | 0.01 | 0.00 | | | | | | | | | | | | | | | | | | |
| Sugar oligomers | MT/hr | 1.59 | 0.04 | | | | | | | | | | | | | | | | | | |
| Lignin (dissolved) | MT/hr | 0.16 | 0.00 | | | | | | | | | | | | | | | | | | |
| Acetic acid | MT/hr | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | | | | | | | | | | 0.00 | | 0.00 | | |
| Formic acid | MT/hr | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | | | | | | | | | | 0.00 | | 0.00 | | |
| Furfural | MT/hr | 0.04 | 0.00 | 0.00 | 0.05 | 0.05 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.00 | 0.00 | 0.00 | | |
| Levulinic acid | MT/hr | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | | | | | | | | | | | | | | |
| 5-HMF | MT/hr | 0.04 | 0.00 | | | | | | | | | | | | | | | | | | |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | 6.91 | 0.16 | | 0.00 | 0.00 | 0.00 | | | | | | | | | | | | | | |
| Other organics | MT/hr | 0.90 | 0.02 | | 0.00 | 0.00 | 0.00 | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | 0.00 | 0.00 | | | | | | | | | | | | | | | | | | |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | 1.19 | 0.03 | | | | | | | | | | | | | | | | | | |
| Carbon dioxide | MT/hr | 0.00 | 0.00 | 0.61 | 0.02 | 0.00 | 0.00 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | | | | | 18.26 | 18.23 | 0.02 | | |
| Methane | MT/hr | | | | | | | | | | | | | | | | | | | | |
| O2 | MT/hr | | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | | | | 0.12 | 0.12 | 0.00 | | |

## Electronic supplementary material Table 1S
## Mass and energy balances

| | Unit | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream | | 161 | 162 | 163 | 164 | 165 | 166 | 167 | 168 | 169 | 170 | 171 | 172 | 173 | 174 | 175 | 176 | 177 |
| Total flow | MT/hr | 0.50 | 56.39 | 56.39 | 85.58 | 147.18 | 302.41 | 29.41 | 4.82 | 3.56 | 1.88 | 293.33 | 13.25 | 13.25 | 85.58 | 194.50 | 0.00 | 9.07 |
| Temperature | C | 240 | 20 | 71 | 187 | 171 | 176 | 20 | 29 | 25 | 25 | 454 | 273 | 190 | 273 | 240 | 0 | 279 |
| Pressure | atm | 9.5 | 6.0 | 6.0 | 11.5 | 8.0 | 62.2 | 1.0 | 1.0 | 1.0 | 1.0 | 59.9 | 13.0 | 12.3 | 13.0 | 9.5 | 0.0 | 62.2 |
| Vapor fraction | | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.0 | 1.0 | 1.0 | 0.0 | 0.0 |
| Enthalpy | GJ/hr | -6.5 | -894.7 | -883.2 | -1292.3 | -2235.2 | -4584.3 | 0.0 | -64.6 | -16.5 | -8.7 | -3687.2 | -171.5 | -199.9 | -1107.3 | -2529.1 | 0.0 | -131.3 |
| Glucan | MT/hr | | | | | | | | | | | | | | | | | |
| Xylan | MT/hr | | | | | | | | | | | | | | | | | |
| Mannan | MT/hr | | | | | | | | | | | | | | | | | |
| Galactan | MT/hr | | | | | | | | | | | | | | | | | |
| Arabinan | MT/hr | | | | | | | | | | | | | | | | | |
| Lignin (insoluble) | MT/hr | | | | | | | | | | | | | | | | | |
| Acetate groups | MT/hr | | | | | | | | | | | | | | | | | |
| Rejects | MT/hr | | | | | | | | | | | | | | | | | |
| Enzyme | MT/hr | | | | | | | | | | | | | | | | | |
| Cell mass | MT/hr | | | | | | | | 1.01 | | | | | | | | | |
| TOPO | MT/hr | | | | | | | | | | | | | | | | | |
| Other insolub. solids | MT/hr | | | | | | | 14.71 | | | | | | | | | | |
| Water | MT/hr | 0.50 | 56.39 | 56.39 | 85.58 | 147.18 | 302.41 | 14.71 | 3.81 | | | 293.33 | 13.25 | 13.25 | 85.58 | 194.50 | | 9.07 |
| Ethanol | MT/hr | | | | | | | | | | | | | | | | | |
| Glucose | MT/hr | | | | | | | | | | | | | | | | | |
| Other C6 sugars | MT/hr | | | | | | | | | | | | | | | | | |
| Xylose | MT/hr | | | | | | | | | | | | | | | | | |
| Arabinose | MT/hr | | | | | | | | | | | | | | | | | |
| Sugar oligomers | MT/hr | | | | | | | | | | | | | | | | | |
| Lignin (dissolved) | MT/hr | | | | | | | | | | | | | | | | | |
| Acetic acid | MT/hr | | | | | | | | | | | | | | | | | |
| Formic acid | MT/hr | | | | | | | | | | | | | | | | | |
| Furfural | MT/hr | | | | | | | | | | | | | | | | | |
| Levulinic acid | MT/hr | | | | | | | | | | | | | | | | | |
| 5-HMF | MT/hr | | | | | | | | | | | | | | | | | |
| Undecane | MT/hr | | | | | | | | | | | | | | | | | |
| Other org. dissolved solids | MT/hr | | | | | | | | | | | | | | | | | |
| Other organics | MT/hr | | | | | | | | | | | | | | | | | |
| Sulfuric acid | MT/hr | | | | | | | | | | | | | | | | | |
| Ammonia | MT/hr | | | | | | | | | | | | | | | | | |
| Other inorg. dissolved soli | MT/hr | | | | | | | | | | | | | | | | | |
| Carbon dioxide | MT/hr | | | | | | | | | | | | | | | | | |
| Methane | MT/hr | | | | | | | | | 3.56 | 1.88 | | | | | | | |
| O2 | MT/hr | | | | | | | | | | | | | | | | | |

**Electronic supplementary material Table 2S** Electricity consumption in different process areas and pieces of equipment

| Process area | Electricity MW | Based on |
|---|---|---|
| Feed handling | 2.5[b] | [50] |
| Pretreatment[a] | | |
| Cooking | 2.5[b] | [50] |
| Pulp washing | 1.5[b] | [50] |
| Reject screening | 3.3[b] | [50] |
| Pumps | 0.8 | [37] |
| Agitators | 0.3 | [36,37][c] |
| Compressors, screws, conveyors | 0.6 | [36,37][c] |
| Total | 8.9 | |
| Hydrolysis, fermentation, and EtOH purification | | |
| Pumps | 0.5 | [36][c] |
| Agitators | 1.2 | [36][c] |
| Compressors, screws, conveyors, mixers | 0.6 | [36][c] |
| Molecular sieves | 0.1 | [36][c] |
| Total | 2.4 | |
| Wastewater treatment | 7.4 | [36][d] |
| Storage | 0.01 | [36][d] |
| Boiler & turbogenerator | 1.6 | [36][e] |
| Utilities | | |
| Cooling water pump & tower system | 2.7 | [36][f] |
| Chilled water system | 1.9 | [36][f] |
| Instrument air | 0.2 | [36][d] |
| Process water | 0.1 | [36][d] |
| Sterile water & CIP/CIS systems | 0.3 | [36][d] |
| Total | 5.2 | |
| Total electricity consumption | 27.9 | |

[a] Including cooking, solvent, furfural, and acetic acid recoveries and conditioning of the hemicellulosic sugar stream

[b] Consumptions assumed comparable to conventional kraft pulping

[c] Values from [36] scaled based on mass flows

[d] Values assumed similar to those in [36]

[e] Values from [36] scaled based on heat flow

[f] Values from [36] scaled based on cooling/chilled water demand

# Publication IV

Kautto, J., Realff, M.J., Ragauskas, A.J. and Kässi, T.
**Economic analysis of an organosolv process for bioethanol production**

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# Economic Analysis of an Organosolv Process for Bioethanol Production

Jesse Kautto,[a,b,]* Matthew J. Realff,[c] Arthur J. Ragauskas,[d] and Tuomo Kässi [b]

In a previous paper, conceptual process design, simulation, and mass and energy balances were presented for an organosolv process with a hardwood feed of 2350 metric tons (MT) per day and ethanol, lignin, furfural, and acetic acid production rates of 459, 310, 6.6, and 30.3 MT/day, respectively. In this paper, the investment and operating costs of the process and the minimum ethanol selling price (MESP) to make the process economically feasible were estimated. The total capital investment of the plant was approximately 720 million USD. Lignin price was found to affect the MESP considerably. With a base case lignin price of 450 USD/MT, the MESP was approximately 3.1 USD per gallon (gal). Higher lignin price of 1000 USD/MT was required to equal the MESP with the December 2013 ethanol market price (2.0 USD/gal). In addition to lignin price, the MESP was found to be strongly affected by feedstock, enzyme, and investment costs. Variations in feedstock and investment costs affected the MESP by approximately 0.2 and 0.5 USD/gal, respectively. Changing the enzyme dosage and price from base case estimate of 5270 USD/MT and 0.02 g/g cellulose to more conservative 3700 USD/MT and 0.06 g/g cellulose, respectively, increased the MESP by 0.59 USD/gal.

*Keywords: Organosolv; Economic assessment; Pretreatment; Bioethanol; Lignin; Simulation*

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## INTRODUCTION

The production of bioethanol from lignocellulosic material has been seen as a potential way to reduce carbon dioxide emissions and dependence on fossil fuels (Hamelinck *et al.* 2005). In the production of this second-generation bioethanol, the natural recalcitrance of lignocellulosic material (Himmel *et al.* 2007) is overcome in a pretreatment step by disrupting the cell structure of the material, enabling the hydrolysis of cellulose to monomer glucose. The monomeric sugars are then fermented to ethanol, and the fermentation beer is dehydrated to a pure ethanol product. For the pretreatment step, several different methods, such as dilute acid, hot water, and steam explosion have been proposed (Hamelinck *et al.* 2005; Mosier *et al.* 2005). Since it has also been considered one of the most expensive processing steps (Mosier *et al.* 2005), the choice and development of a pretreatment method could have a considerable effect on the economics of bioethanol production.

One possible pretreatment method is organosolv pulping in which lignin is dissolved in an organic solvent. The process was originally considered as a pulping method for the production of paper pulp (Hergert 1998; Aziz and Sarkanen 1989), but it has recently gained interest as a potential pretreatment method in bioethanol production (Pan *et al.* 2005; 2006). Although it has generally been considered as an expensive pretreatment method (Zhao *et al.* 2009), the use of organic solvents enables the recovery of a pure lignin product and potentially other co-products (Pan *et al.* 2005; 2006). The production of co-products could possibly offset the perceived high cost of organosolv pulping. The operation of pilot or demonstration scale organosolv biorefineries by companies such as Chempolis, CIMV, and Lignol Innovations (Chempolis 2009; Lignol 2009; CIMV 2013a) can be considered as indications of the interest in organosolv technology.

Several techno-economic studies have been carried out to analyze the technical and economic feasibility of different second-generation bioethanol production processes and to compare different pretreatment methods (Eggeman and Elander 2005; Kazi *et al.* 2010; Humbird *et al.* 2011; Tao *et al.* 2011). These studies are typically based on simulation models, with their key parameters derived from laboratory or pilot scale experiments. The economic feasibility of bioethanol production is often characterized in these studies by the minimum ethanol selling price (MESP) (Humbird *et al.* 2011) covering the operating and capital costs of production and making a certain return on the invested capital.

A recent National Renewable Energy Laboratory (NREL) technical report (Humbird *et al.* 2011) presented a detailed techno-economic study on the production of bioethanol from corn stover based on dilute acid pretreatment and enzymatic hydrolysis. With a corn stover feed of 2000 dry metric tons (MT) per day and a price of 64.5 USD/dry MT, and an in-house enzyme production cost of 0.34 USD per gallon (gal) of ethanol produced, they arrived at an MESP of 2.15 USD/gal. Other techno-economic studies include the studies of Eggeman and Elander (2005), Kazi *et al.* (2010), and Tao *et al.* (2011), which compared the economics of different pretreatment technologies. All of these studies assumed a feedstock feed of 2000 MT/day. Depending on the pretreatment technology, the capital costs were in the range of 164 to 212 million US dollars (MUSD) (Eggeman and Elander 2005), 327 to 391 MUSD (in 2007 dollars) (Kazi *et al.* 2010), and 325 to 385 MUSD (in 2007 dollars) (Tao *et al.* 2011). The MESPs were in the range of 1.3 to 1.7 (Eggeman and Elander 2005), 3.4 to 4.5 (Kazi *et al.* 2010), and 2.7 to 4.1 USD/gal (Tao *et al.* 2011). A more extensive review of recent techno-economic studies was presented in the NREL study (Humbird *et al.* 2011). In this review, the MESPs were found to vary between different studies in the range of approximately 0.6 to 4.6 USD/gal of ethanol produced, with the variations being largely explained by differences in assumed feedstock prices, process yields, and co-product credits. In sensitivity analyses presented by Kazi *et al.* (2010) and Humbird *et al.* (2011), MESPs were found to be very sensitive to variations in capital costs (Humbird *et al.* 2011), enzyme cost, and cellulose to glucose conversion in enzymatic hydrolysis (Kazi *et al.* 2010; Humbird *et al.* 2011), and feedstock cost (Kazi *et al.* 2010).

A few economic assessments on organosolv processes have also been published. For example, van der Linden *et al.* (2012) reported in a conference presentation the income distributions, capital costs, operating costs, and payback times for an ethanol-organosolv biorefinery producing cellulose pulp, lignin, and furfural at assumed prices of 350 EUR/MT (455 USD/MT, using an EUR-USD exchange rate of 1.3 both here and elsewhere in this work), 750 EUR/MT (975 USD/MT), and 625 EUR/MT (813 USD/MT), respectively, from various feedstocks. At a feedstock feed of 150,000 MT/year, the total fixed capital was estimated to be 80 to 87 million EUR (104 to 113 MUSD) with the organosolv reactor section being the single most expensive section in the process. The payback time was found to be in the approximate range of 6 to 7 years. Dias *et al.* (2011) compared a first generation sugarcane juice bioethanol process to different integrated first and second-generation bioethanol processes (both sugarcane juice, bagasse, and trash). The second-generation process was based on different pretreatment methods. An organosolv-based process was found to result in investment and production costs and internal rates of return that were relatively similar to those of a steam explosion-based process. Lignin from the organosolv pulping process was assumed to be combusted. González Alriols *et al.* (2010) presented an organosolv biorefinery process where an ultrafiltration separation system was used to produce lignin fractions with different molecular weights. Capital and operating costs were calculated for the ultrafiltration system, resulting in a production cost of 52 EUR/MT (68 USD/MT) of lignin. Mabee *et al.* (2006) estimated the mass and energy balances and investment and operating costs for bioethanol production processes based on acid-catalyzed ethanol organosolv and sulfur dioxide-catalyzed steam explosion pretreatments of Douglas fir. They compared the processes and found the total production costs of the organosolv process to be lower. They further found the co-product lignin sales price to significantly affect the production costs. Only relative costs were, however, presented in these analyses. Absolute figures enabling the economic assessment of the organosolv process were not provided. Parajó and Santos (1995) presented a techno-economic study on the acid-catalyzed acetic acid pulping of *Eucalyptus globulus* wood for the production of paper pulp and co-products. Based on a proposed flowsheet and mass and energy balances, they calculated the investment and operating costs of the process and further assessed its profitability. They varied the lignin price and found the process to be clearly unprofitable and non-competitive with other paper pulp production processes if the lignin was sold at its fuel value. The process was closer to profitability if the lignin was sold at a price corresponding to its use as an asphalt extender and profitable at higher prices, corresponding to its use as a dispersing agent, intermediate in polymer manufacture or as a phenol extender in phenol-formaldehyde resins.

Although economic assessments of organosolv processes have been published (Parajó and Santos 1995; Mabee *et al.* 2006; González Alriols *et al.* 2010; Dias *et al.* 2011; van der Linden *et al.* 2012), no comprehensive studies analyzing the economic feasibility of ethanol production as well as the effect of co-products on the economics based on detailed flowsheets and balances are known. This paper is a continuation of a previous paper (Kautto *et al.* 2013) in which the technical and simulation aspects of an acid-catalyzed ethanol organosolv process for the production of bioethanol and co-products, lignin, acetic acid, and furfural, from lignocellulosic material were examined. Based on the detailed process flowsheets and mass and energy balances presented in the previous paper, the economics of the organosolv biorefinery will be analyzed in this paper. The estimated capital costs including the sizing and costing of the main equipment and the operating costs of the process will first be presented. The MESP for a base case scenario will then be calculated and the effect of variations in main technical and economic attributes on the MESP will be analyzed in sensitivity analyses. The effect of the recovery of co-products on the feasibility of the process will also be discussed. Whenever applicable, the technical analysis of the organosolv process presented earlier

(Kautto *et al.* 2013) followed closely the NREL dilute acid pretreatment study (Humbird *et al.* 2011). Assumptions adopted in this economic analysis will also be similar to those of the NREL study (Humbird *et al.* 2011), making the two processes comparable. The economic feasibility of the organosolv process will therefore be compared to the dilute acid process. Their relative differences will be discussed, and the conditions under which the organosolv process could be competitive will be analyzed.

## MATERIALS AND METHODS

### Overview of the Studied Organosolv Biorefinery Concept

As discussed in the *Introduction*, the economic analysis carried out in this paper was based on a technical analysis presented previously (Kautto *et al.* 2013). The detailed flowsheets and mass and energy balances of the previous paper were used to estimate the operating and capital costs and revenues of the process.

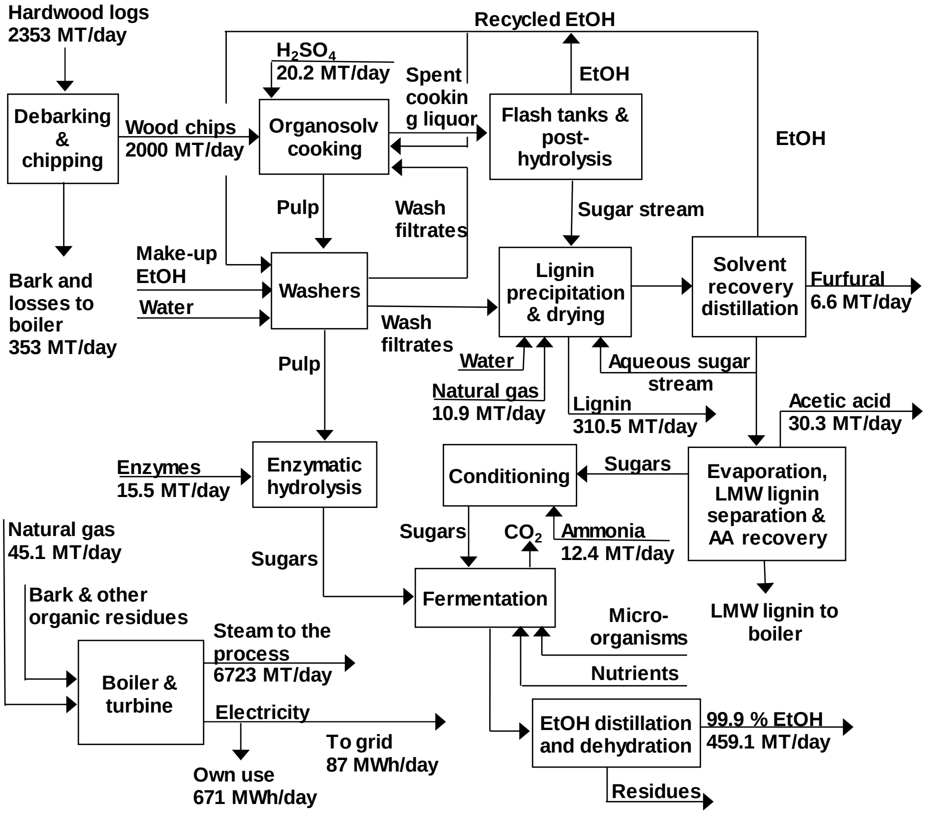

**Fig. 1.** Simplified block diagram of the modeled ethanol organosolv process with the main process steps and input and output flows

With an intake of 2350 dry MT/day of undebarked hardwood, resulting in 2000 MT/day of debarked chips fed to cooking, the production rates of ethanol, lignin, furfural, and acetic acid were 459.1, 310.5, 6.6, and 30.3 MT/day, respectively. A small amount of natural gas was needed to cover the steam balance of the process. The hardwood was assumed to be hybrid poplar. A simplified block diagram of the modeled process with the main process steps and input and output flows is presented in Fig. 1. More detailed process and balance information can be found in the previous study (Kautto *et al.* 2013). For the purposes of the economic assessment, the plant was assumed to be located in the USA.

## Investment Costs

Due to the relatively high level of detail of the NREL study (Humbird *et al.* 2011) and significant similarities between that and our study in several process areas, most investment costs were assessed based on data of that study. The organosolv process plant was divided into process areas for investment cost analysis. The costs of areas assumed similar to the NREL study (Humbird *et al.* 2011) were estimated by directly scaling the costs from that study on a process area basis. These areas were wastewater treatment, storage, utilities, and boiler and turbine. The costs of all the other process areas were estimated on an individual equipment basis, using the equipment costs, installation factors, and scaling exponents of the NREL study (Humbird *et al.* 2011) as well as the Aspen Process Economic Analyzer software (AspenTech 2011), industry estimates, and a previous NREL study from 2002 (Aden *et al.* 2002). Where Aspen Process Economic Analyzer was used in estimating the equipment costs, the installed costs of these pieces of equipment were calculated using installation factors of the NREL study (Humbird *et al.* 2011).

Material of construction in most areas was either SS304 or SS316, depending on the process conditions. All prices were indexed to the year of 2013 using Chemical Engineering Plant Cost Index (CEPCI). A preliminary value of April 2013 was used as the value for 2013 (Chemical Engineering 2013). Table 1 reports the process areas, their descriptions, and the costing bases.

After assessing the installed equipment costs of different process areas, the costs of warehouse, site development, additional piping, different indirect costs, and other costs as well as the amount of working capital were calculated following the data and methodology presented in the NREL study (Humbird *et al.* 2011). The costs of warehouse, site development, and additional piping were calculated in the NREL study (Humbird *et al.* 2011) as a percentage of the inside battery limits (ISBL) investment cost. In this study the ISBL was set to consist of process areas of feed handling, pretreatment and lignin recovery, solvent and furfural recovery, conditioning of the hemicellulosic sugar stream, acetic acid recovery, enzymatic hydrolysis and fermentation, and ethanol product and solids recovery.

The indirect costs were calculated in the NREL study (Humbird *et al.* 2011) as a percentage of the total direct costs. The working capital was calculated as a percentage of the fixed capital investment (the sum of direct and indirect costs). All the percentages used in this study are presented in Table 4 in the subsection *Base case economic assessment*.

**Table 1.** Process Areas and Bases of Costing

| **Process area** | **Description** | **Basis of costing** | **Source and scaling basis** |
|---|---|---|---|
| Feed handling | Wood yard (wood receiving, debarking, and chipping) | Process area | Industry estimate |
| Pretreatment and lignin recovery | Cooking, pulp washing, post hydrolysis, precipitation, and drying of lignin | Individual equipment | Industry estimate, (AspenTech 2011; Humbird *et al.* 2011;) |
| Solvent and furfural recovery | Solvent and furfural recovery columns | Individual equipment | (AspenTech 2011; Humbird *et al.* 2011;) |
| Conditioning of the hemicellulosic sugar stream | Evaporation, separation of low molecular weight lignin, ammonia treatment | Individual equipment | (Aden *et al.* 2002; AspenTech 2011; Humbird *et al.* 2011;) |
| Acetic acid recovery | Extraction of acetic acid from evaporator condensates, distillation to pure acetic acid product | Individual equipment | (AspenTech 2011) |
| Hydrolysis and fermentation | Enzymatic hydrolysis and fermentation to ethanol | Individual equipment | (Humbird *et al.* 2011) |
| Ethanol product and solids recovery | Distillation of pure ethanol product, filtration of distillation bottoms solids | Individual equipment | (Humbird *et al.* 2011) |
| Wastewater treatment | Anaerobic and aerobic treatment systems | Process area | (Humbird *et al.* 2011), assumed similarly sized |
| Storages | End-product and raw material storages | Process area | (Humbird *et al.* 2011), assumed similarly sized |
| Boiler and turbine | Combustion of organic residues and purchased natural gas and generation of steam and electricity | Process area | (Humbird *et al.* 2011), scaled on the amount of combustion heat |
| Utilities | Cooling and chilled water, plant/instrument air, and process water systems | Process area | (Humbird *et al.* 2011), cooling and chilled water systems scaled on cooling duty, everything else assumed similar |

## Annual Cash Flows

### *Cost of feedstock*

Various types of biomass could be utilized in the production of second generation ethanol, including agricultural residues such as corn stover, straws and bagasse, forest biomass and woody residues (hardwoods and softwoods, various forest residues, and mill residues from the forest industry), and herbaceous grasses such as switchgrass (see Huang *et al.* 2009; U.S. Department of Energy 2011). Due to differences in composition (Santos *et al.* 2012) and delivered cost (Huang *et al.* 2009; Gnansounou and Dauriat 2010; Gonzalez *et al.* 2011), the type of feedstock has an effect on the economics of bioethanol production (Huang *et al.* 2009; Gnansounou and Dauriat 2010; Gonzalez *et al.* 2011; Santos *et al.* 2012). Moreover, various feedstocks have different availabilities and delivered costs depending on the exact location of the biomass processing facility.

In the technical part of this study, mass and energy balances over the organosolv process were calculated assuming a hybrid poplar feedstock (Kautto *et al.* 2013). Although organosolv pretreatment has been demonstrated to be suitable for a wide range of feedstocks (see Pan *et al.* 2005 for softwood, Pan *et al.* 2006 for hardwood, and Mesa *et al.* 2010 for sugarcane bagasse), the economic analysis is also carried out assuming the same feedstock. For bioenergy and biofuel production, various poplar prices have been reported in the literature. Table 2 lists some reported price estimates.

**Table 2.** Reported Poplar Prices

| **Reference** | **Poplar price/cost** | **Location and plant capacity** |
|---|---|---|
| Phillips *et al.* 2007 | Delivered cost target of 35 USD/dry short ton of wood chips (in 2005 dollars, approximately 39 USD/dry MT) | 2000 dry MT/day |
| Huang *et al.* 2009 | Delivered cost of cropland grown hybrid poplar chips estimated at 104.65 USD/dry MT (in 2005 dollars), with the cost consisting of land, production, harvest, chipping, fixed (independent of distance) transportation, and variable (dependent of distance) transportation costs of 20.50, 38.64, 16.0, 14.0, 4.55, and 10.96 (with a collection radius slightly below 60 km) USD/dry MT, respectively | Minnesota, 2000 dry MT/day |
| Jones *et al.* 2009 | Hybrid poplar wood chip delivered price of 50.7 USD/dry short ton (in 2007 dollars, 55.9 USD/dry MT) | 2000 dry MT/day |
| Gnansounou and Dauriat 2010 | Delivered cost of poplar estimated at 140.4 USD/dry ton (in 2007 dollars), with the non-transport costs being 123.3 and transport costs 17.1 USD/dry ton (average collection radius 40 km) | 1636 dry ton/day, |
| Khanna and Huang 2010 | Of the studied three states, farm-gate break-even price of poplar chips was found to be the lowest in Michigan, being in the range 88 – 95 USD/dry MT (in 2007 dollars) when grown on marginal land and 106 – 115 USD/dry MT when grown on cropland. The break-even prices were found to be sensitive to changes in biomass yield and harvest cost both on marginal and cropland and to changes in the prices of corn and soybean on cropland (corn-soybean rotation was assumed to be the most profitable use of land and therefore determined the opportunity cost of cropland). | Michigan, Illinois, Oklahoma |
| Berguson *et al.* 2010 | Delivered costs of hybrid poplar chips estimated to be in the range of 70 – 100 USD/dry short ton (approx. 77 – 110 USD/dry MT) in Pacific Northwest, with the exact value depending on the assumed land costs and discount rates. The costs consisted of 27% land, 9% establishment, 28% crop care and management, 24% harvest, and 12% transport costs. The prices were estimated to be in the same range also in Minnesota. | Pacific Northwest, Minnesota, average one-way hauls 30-65 miles |

The study of Berguson *et al.* (2010) was followed in setting the feedstock price. Since hardwood feedstock was assumed to be debarked and chipped onsite in this organosolv study (Kautto *et al.* 2013) and Berguson *et al.* (2010) reported the cost of hybrid poplar as chipped, a minor conversion was made to the costs of Berguson *et al.* (2010). The base case price of the undebarked poplar wood was assumed in this study to be 85 USD/dry MT delivered to the plant gate, and the feedstock price was assumed to vary in the range of 70 to 100 USD/dry MT in sensitivity analyses. The effect of these changes on the MESP is discussed in more detail in subsection *Sensitivity analyses*.

### *Cost of enzymes*

The cost contribution of enzymes in techno-economic second generation ethanol studies has typically been reported either on a very aggregated level as a cost contribution per gallon of ethanol produced or calculated based on assumed price (or production cost) and loading of enzymes. A wide range of enzyme cost contributions have been assumed in these studies, including a cost goal of 0.1 USD/gal (approximately 1.5 USD/kg cellulase at a loading of 0.02 g cellulase/g cellulose) in the 2002 NREL study (Aden *et al.* 2002), future price projection of 0.15 USD/gal in (Eggeman and Elander 2005), 0.25 USD/gal (Tao *et al.* 2011), and costs of 0.71, 0.35, and 2.09 USD/gal reflecting a loading of 0.0313 g protein/g cellulose in untreated biomass and a base case enzyme price of approximately 5.1 USD/kg derived from an enzyme production model and lower and higher price scenarios of 2.6, and 14.6 USD/kg, respectively (Kazi *et al.* 2010).

Some studies have presented more detailed analysis on the economics of enzyme production. Klein-Marcuschamer *et al.* (2011) carried out a techno-economic analysis of cellulase production from steam-exploded poplar wood by fungus *Trichoderma reesei*. At a cellulase production capacity enough to supply a cellulosic ethanol plant processing 1700 dry MT of corn stover per day (Klein-Marcuschamer *et al.* 2010), a poplar cost of 60 USD/MT, residence time of 192 h in aerobic fermentation, and a final enzyme concentration after filtration of 150 g/L, they arrived at a baseline cost of enzymes of 10.14 USD/kg (in 2010 dollars). This corresponded to a cost contribution of 1.47 USD/gal ethanol at a loading of 0.02 g enzyme/g cellulose. The enzyme production cost was found to be largely governed by capital (48% of total) and feedstock costs (28%). An on-site enzyme production process was also modeled in the NREL study (Humbird *et al.* 2011). Using glucose as the sugar source in fermentation, they arrived at a somewhat lower enzyme cost of 4.24 USD/kg (in 2007 dollars), which resulted in a cost contribution of 0.34 USD/gal ethanol at a loading of 0.02 g enzyme protein/g cellulose. The key cost contributors were found to be the sugar (57% of total) and capital costs (21%). The differences in enzyme production costs and cost structures between the NREL study (Humbird *et al.* 2011) and Klein-Marcuschamer *et al.* (2011) reflect at least partially different feedstocks (sugar sources) used in enzyme production.

Although the NREL enzyme cost could be considered rather optimistic, it was here used as a basis to calculate the base case enzyme cost to align this study with the NREL study. Based on the enzyme production cost breakdown presented in the NREL study (glucose, other nutrients, electricity, and fixed and capital costs), the cost was in this study indexed to the year 2013 using the plant cost index, the 2013 glucose price (USDA 2013), producer price index for industrial chemicals, and the 2013 electricity price. This resulted in an enzyme cost of 5270 USD/MT. Also, the enzyme loading (0.02 g enzyme/g cellulose) was assumed to be the same as in the NREL study. The enzyme was assumed to be supplied by a separate operator at the indexed enzyme production cost. Price estimates (3700 USD/MT) and dosing suggestions (0.06 g enzyme/g cellulose) from an enzyme provider from 2011 (Novozymes 2011) were used as a more conservative scenario in sensitivity analyses.

### *Other assumptions related to variable and fixed costs and revenues*

There is no commercial production and therefore no existing market for the quantities of organosolv lignin that would be generated through such large scale production as studied in this paper. Furthermore, there is a wide range of products that could be assumed to be produced from organosolv lignin. Estimating the market price for the lignin is therefore difficult. The price of lignin was assumed to be 450 USD/MT in the base case scenario. This is in line with Gosselink (2011) who reported kraft (lignin separated from kraft pulp cooking liquor), soda (lignin from soda pulp cooking liquor), and organosolv lignin values in the range of 350 to 500 EUR/MT (455 to 650 USD/MT).

Higher price assumptions were reported by Baker (2010) in a presentation on the use of organosolv and kraft lignins in the production of carbon fibers (lignin price below 1100 USD/MT), by van der Linden *et al.* (2012) (975 USD/MT), and by Rushton (2012) in a presentation on Lignol's biorefining revenue scenarios (1900 USD/MT). Indication of a higher lignin price can also be drawn from the earlier activities of a company called Repap. The company operated a 30 MT/day organosolv pulping demonstration plant (so called Alcell process) intermittently from 1989 to 1996, producing more than 3700 MT of lignin and selling most of it for its use for example in phenolic resins (Pye 2010a). Repap further planned a larger, 450 MT/day organosolv pulping plant, and undertook studies to evaluate markets for the larger lignin output. According to Pye (2010a), the studies suggested that larger quantities of organosolv lignin could have been sold at an average price close to the price of phenolic resin (see subsection *Sensitivity analyses* for the current market price). Although some of the literature and earlier experience seem to suggest that relatively high prices could be obtained for organosolv lignin, the more conservative price assumption of 450 USD/MT, representing the lower end of the price range presented in the literature, was seen as justifiable in this paper due to lack of price data of current, larger scale sales of organosolv lignin. The pricing of lignin as well as the effect of changes to the assumed lignin price are discussed in more detail in subsection *Sensitivity analyses*.

The prices of chemicals were estimated mainly based on the NREL study (Humbird *et al.* 2011). Other sources were used for acetic acid (Kelley 2013), furfural (Arato *et al.* 2005), and kerosene (Dennis *et al.* 2013). The chemical prices were indexed to the year 2013 using CEPCI producer price index for industrial chemicals (Chemical Engineering 2013). The prices of natural gas and electricity represented price level in December 2013 and were based on data of U.S. Energy Information Administration (2013a,b). Other cost items, including salaries, labor burden, maintenance, and property insurance were estimated based on the NREL study (Humbird *et al.* 2011). The amount of personnel was assumed similar to that in the NREL study (Humbird *et al.* 2011), and the labor cost was indexed to 2013 using labor cost index for the chemical industry (Bureau of Labor Statistics 2013).

## MESP Analysis

Following assumptions made in the NREL study (Humbird *et al.* 2011), plant online time of approximately 350 days per year was assumed in this study. The plant was assumed to be in full operation for 30 years. Table 3 presents the assumed time-table and cash flows for planning and engineering, construction, and start-up.

**Table 3.** Plant Planning and Engineering, Construction, and Start-up Times

| Phase | Time, months | Cash flow |
|---|---|---|
| Planning and engineering | 0 – 12 | 8% of project investment |
| Construction | 12 – 24<br>24 – 36 | 60% of project investment<br>32% of project investment +working capital |
| Start-up | 36 – 39 | 50% of production<br>75% of variable costs<br>100% of fixed costs |
| Full production | 39 → | |

Based on the estimated investment costs and annual cash flows, the economic feasibility of the organosolv plant was assessed using the MESP, which is widely used in the literature studying different bioethanol production concepts. The MESP is the selling price of ethanol that makes the net present value of the ethanol process equal to zero (Humbird *et al.* 2011) so that the ethanol sales revenue fully compensates for both the operating and capital costs of the project with a given discount rate. The MESP calculation was done following the recent and earlier NREL studies (Aden *et al.* 2002; Humbird *et al.* 2011). The discount rate was set to 10%, capital investment was assumed to be 40% equity financed, the interest on loan was 8% and it was paid back in 10 years, corporate tax rate was 35%, and a 150% declining base depreciation method with a 20-year recovery period was adopted for the steam and power production plant and a 200% declining base with a 7-year recovery for the rest of the equipment.

As either price information from 2013 or prices indexed to 2013 price level using CEPCI index values were used throughout this study, the dollars used in this study can be considered as 2013 dollars.

### Technical Parameters Varied in Sensitivity Analyses

The economic assumptions described above and the technical assumptions described in the companion paper (Kautto *et al.* 2013) outline the base case scenario of the modeled organosolv process. Due to uncertainties inherent in a conceptual process simulation study like this, sensitivity analyses were run to estimate the effect of changes in some main parameters on the MESP of the studied organosolv concept. Both technical (internal) and exogenous (external, market-related) parameters were analyzed. The lignin sales price and feedstock, enzyme, and investment costs were selected as exogenous parameters, and parameters related to enzymatic hydrolysis, fermentation, and energy consumption were selected as technical parameters. Regarding the market-related parameters, variations in feedstock and enzyme costs were discussed in subsections *Cost of feedstock* and *Cost of enzymes*, investment costs were assumed to vary by 30%, and the sales price of lignin will be discussed separately in subsection *Sensitivity analyses*. The rationale for the selection of the technical parameters and their variation is discussed below.

Ethanol organosolv pulps have generally been found to exhibit good response to enzymatic hydrolysis (Pan *et al.* 2005; 2006). Pan *et al.* (2006) presented how low lignin content organosolv pulps exhibit significantly better response to enzymatic hydrolysis than higher lignin content steam-exploded wood. With approximately the same enzyme loading (20.9 mg cellulase and 5.7 mg β-glucosidase per g cellulose) and same hydrolysis time of 36 h (but with a significantly lower solids content), Pan *et al.* (2006) reported hybrid poplar pulp prepared at the same conditions adopted in this study to exhibit a conversion efficiency of cellulose to glucose of approximately 96%. The enzymatic conversion of organosolv-cooked hybrid poplar might therefore be higher than that of dilute acid-pretreated corn stover of the NREL study (Humbird *et al.* 2011) (cellulose to glucose conversion of 90%). The effect of improved enzymatic hydrolysis on the economics of the organosolv process was studied by setting sugar conversion yield 6 percentage points higher for all carbohydrates. On the other hand, due to enzyme inhibition and deactivation caused by soluble sugars, furfural, hydroxymethyl furfural, organic acids, and phenolics at higher solids contents (see Kim *et al.* 2011), the conversion rates in industrial scale enzymatic hydrolysis could be significantly lower than those reported by Pan *et al.* (2006). Therefore, a conversion of both cellulose and hemicelluloses to sugars of 80% was adopted as a more conservative scenario for the enzymatic hydrolysis.

In addition to assuming an improved enzymatic hydrolysis as described above, a higher overall sugar recovery could have also been achieved by assuming a higher carbohydrate recovery in the cooking section. As discussed in the previous paper (Kautto *et al.* 2013), the carbohydrate recovery was assumed to be 84% based on Pan *et al.* (2006), being considerably lower than that in the NREL study (Humbird *et al.* 2011) (approximately 98%). Mabee *et al.* (2006) reported a higher recovery in the organosolv cooking of softwood (90% for both glucose and hemicelluloses), suggesting that a higher carbohydrate recovery could be achievable. Improved carbohydrate recovery was, however, not specifically studied in the sensitivity analyses since the effect of such a change would be similar to that of the improved enzymatic hydrolysis.

Mannose and galactose were not assumed to be fermented by the fermenting organism *Zymomonas mobilis*, as outlined in the NREL study (Humbird *et al.* 2011). The fermentation of these sugars has, however, been assumed in several studies (see Aden *et al.* 2002). On the other hand, the fermentation of xylose and other hemicellulosic sugars has generally proven to be challenging (see Aden *et al.* 2002). In addition, due partially to relatively high temperature and long residence time in organosolv cooking (assumed to be 180 °C and 60 minutes (Kautto *et al.* 2013), based on Pan *et al.* (2006)), and the need to close the cooking mass balance, the aqueous stream from cooking was assumed to contain initially relatively high amounts of sugar degradation products (see discussion in the companion paper (Kautto *et al.* 2013)). Although the amount of these and other inhibitory compounds were assumed to be decreased to a level low enough for fermentation (Kautto *et al.* 2013), residual inhibitory compounds might affect the fermentation, and no experimental data were available on the fermentability of such a stream. The processing of the hemicellulosic sugar stream could also result in greater sugar losses than assumed; therefore, both the effect of fermentation of mannose and galactose and of a lower fermentation yield of hemicellulosic sugars on the economics of the organosolv process were considered.

Due to the preliminary nature of this study, several assumptions had to be made that would have a considerable effect on the steam and electricity consumption of the process. For example, the liquor-to-wood ratio (LTW) was assumed to be 5. With a higher or lower LTW, the amount of solvent and water recycled, and therefore the steam consumption in distillation, would be changed significantly. Also the extent of, and assumptions made in, heat integration would affect the steam consumption. Due to this inherent uncertainty, the effects of changes in the energy consumption of the process were studied. The steam and electricity consumption of the process were changed by 30%. The effects of these changes on the excess electricity production and/or the natural gas demand, and further on the MESP of the process were then analyzed.

## RESULTS AND DISCUSSION

### Base Case Economic Assessment

In the economic assessment of the organosolv process, the capital investment and variable and fixed costs as well as the co-product credits were assessed first. Based on these, the MESP was calculated to analyze the economic feasibility of the organosolv process. Table 4 presents the investment costs of installed equipment as well as the other direct costs, indirect costs, the cost of land, and working capital. The sizing and costing of individual pieces of equipment and process areas as well as the bases of costing are presented in more detail in the supplementary material (Supplementary Table 1).

**Table 4.** Investment Cost Analysis

| Investment cost | MUSD | Investment cost | MUSD |
|---|---|---|---|
| *Installed equipment cost* | | *Indirect costs* | |
| Process areas | | Prorateable expenses | 43 |
| Feed handling | 42 | (10% of TDC) | |
| Pretreatment and lignin recovery | 88 | Field expenses | 43 |
| Solvent and furfural recovery | 31 | (10% of TDC) | |
| Conditioning of the hemicellulosic stream | 19 | Home office and construction | 86 |
| Acetic acid recovery | 12 | (20% of TDC) | |
| Enzymatic hydrolysis and fermentation | 28 | Project contingency | 43 |
| Ethanol product and solids fermentation | 18 | (10% of TDC) | |
| Wastewater treatment | 54 | Other costs (10% of TDC) | 43 |
| Storages | 5 | **Total indirect costs** | **257** |
| Boiler and turbine | 82 | | |
| Utilities | 7 | **Fixed capital investment** | **685** |
| **Total installed equipment cost** | **386** | **(FCI)** | |
| *Other direct costs* | | Land | 3 |
| Warehouse (4% of ISBL) | 10 | Working capital (5% of FCI) | 34 |
| Site development (9% of ISBL) | 21 | | |
| Additional piping (4.5% of ISBL) | 11 | **Total capital investment** | **722** |
| **Total direct costs (TDC)** | **428** | | |

As can be seen in Table 4, the estimated total capital investment was calculated to be 722 MUSD, resulting in a total capital investment per annual ethanol production of 13.4 USD/gal (4490 USD/MT). The organosolv process presented by van der Linden *et al.* (2012) apparently included size reduction, organosolv cooking, solvent, furfural, and lignin recovery as well as pulp washing but no major auxiliary processes. Scaling their capital cost (see *Introduction*) by a scaling exponent of 0.6 to the feedstock flow used in this study resulted in a total capital investment that is well in line with the direct and indirect capital costs (using the percentages for other direct costs and indirect costs presented in Table 4) of the sections feed handling, pretreatment and lignin recovery, and solvent and furfural recovery of this study (both approximately 300 MUSD).

The NREL dilute acid process (Humbird *et al.* 2011) was used in this work as a reference point for the studied organosolv process. The total capital investment of the NREL process indexed to 2013 from their cost year of 2007 would be approximately 458 MUSD. Not unexpectedly, a more complicated flowsheet of the organosolv process with the recovery of solvent and co-products would therefore make the investment costs of this process higher.

The annual variable and fixed costs, co-product revenues as well as the minimum ethanol sales revenue and the according MESP are presented in Table 5 (see Supplementary Tables 2 and 3 for more detailed breakdowns of the variable operating costs and revenues from by-products as well as of the MESP calculation). The minimum annual ethanol sales revenue was 166 MUSD/year. With an ethanol production of 459 MT/day (Kautto *et al.* 2013), this converted to an MESP of 3.07 USD/gal (approximately 1030 USD/MT).

**Table 5.** Annual Variable and Fixed Costs, Revenues, and MESP

| Annual costs | MUSD/a | Annual revenues | MUSD/a |
|---|---|---|---|
| *Variable costs* | | *Revenues from co-products* | |
| Feedstock | 70.1 | Organosolv lignin | 49.0 |
| Chemicals | | Furfural | 3.7 |
| Cellulase | 28.7 | Acetic acid | 6.4 |
| Others | 9.3 | Electricity | 1.6 |
| Natural gas | 4.1 | **Total co-products revenue** | **60.6** |
| Ash disposal | 0.8 | | |
| *Fixed costs* | | *Revenues from ethanol* | |
| Salaries | 2.7 | **Minimum ethanol sales** | **165.5** |
| Labor burden (90% of salaries) | 2.4 | | |
| Maintenance (3% of ISBL) | 7.1 | **MESP** | **3.07** |
| Property insurance | 4.8 | | **USD/gal** |
| **Total variable and fixed costs** | **130.0** | | |

The major cost factors of the process were feedstock and enzyme costs, lignin co-product credit, and capital costs (Table 6).

**Table 6.** Breakdown of MESP to Cost Contributors

| Cost contributor | USD/gal |
|---|---|
| Feedstock | 1.30 |
| Enzyme | 0.53 |
| Other chemicals & ash disposal | 0.17 |
| Natural gas | 0.08 |
| Co-products | |
| Organosolv lignin | -0.91 |
| Furfural | -0.07 |
| Acetic acid | -0.12 |
| Electricity | -0.03 |
| Fixed costs | 0.32 |
| Capital depreciation | 0.42 |
| Tax | 0.24 |
| Average return on investment | 1.14 |
| **Total** | **3.07** |

Due to their smaller production rates, the sales of the other co-products, furfural and acetic acid, had a smaller effect on the MESP than lignin. By allocating the direct investment costs of the pieces of equipment directly related to the production of furfural and acetic acid as well as the indirect investment costs proportional to these direct investment costs, the direct variable operating costs, and the direct revenues to the furfural and acetic acid co-products, the payback period for these products would be approximately 0.2 and 5.2 years, respectively. This would indicate that the recovery of furfural as a side-draw from the ethanol recovery distillation columns and the further purification of furfural by distillation (Kautto *et al.* 2013) could be economically feasible. Due to the relatively low concentration (approximately 0.7 wt-%) of acetic acid in the evaporator condensates and its rather low price, the economic feasibility of recovering the acetic acid through extraction and distillation would be rather uncertain, especially taking into account that no TOPO (trioctyl phosphine oxide, a solvent used in the extraction of acetic acid) was assumed to be lost in the extraction (Kautto *et al.* 2013).

Aligning feedstock costs of the NREL dilute acid study (Humbird *et al.* 2011) with the current organosolv study and indexing other operating costs and investment costs to the year 2013 resulted in an MESP of the NREL process (approximately 2.6 USD/gal) that is relatively close to the base case MESP of the organosolv process (approximately 3.1 USD/gal). This demonstrates that the organosolv pulping process for the production of bioethanol could be competitive, with either a slightly higher price of lignin or lower investment or operating costs. The US market price of ethanol in December 2013 was approximately 2.0 USD/gal (Chicago Mercantile Exchange 2013), indicating that the MESP of the base case organosolv process would need to be somewhat lower or the market price of ethanol higher to make the process economically attractive (not taking into account any policy instruments to support lignocellulosic ethanol). The economic viability of the organosolv process will be further analyzed in the next section.

## Sensitivity Analyses

Parameters used in the sensitivity analyses covered both technical and market-related aspects of the studied organosolv process. The technical parameters (steam and electricity consumption of the process, conversion rates in the enzymatic hydrolysis stage, and conversion rates of hemicellulosic sugars in the fermentation stage) and their expected variations are discussed in section *Technical parameters varied in sensitivity analyses*. The sensitivity of changes of these factors on the MESP is presented in Table 7. C5 sugars in the table refer to hemicellulosic pentoses (xylose and arabinose) and C6 sugars to hexoses (mannose and galactose). Also the effect of changes in the total capital investment and in the discount rate used in MESP calculation are presented in the table. The effects of lignin price and feedstock and enzyme costs are shown separately in Fig. 2.

**Table 7.** Sensitivity of MESP to Technical Assumptions

| Design parameter | Base case | Value in sensitivity analysis | MESP, USD/gal |
|---|---|---|---|
| Steam and power consumption | 6720 MT/day (steam),<br>670 MWh/day (power) | 8740 MT/day,<br>870 MWh/day (+30%) | 3.25 (+0.18) |
| | | 4710 MT/day,<br>470 MWh/day (-30%) | 2.91 (-0.17) |
| Conversion rate in the enzymatic hydrolysis | 90% for cellulose,<br>82% for hemicelluloses | 96% for cellulose, 88% for hemicelluloses (high) | 2.92 (-0.15) |
| | | 80% for cellulose and hemicelluloses (low) | 3.38 (0.30) |
| Conversion rate of hemicellulosic sugars in the fermentation | 85% for C5 sugars, 0% for C6 sugars | 85% for C5 and C6 sugars (high) | 2.88 (-0.19) |
| | | 50% for C5 sugars, 0% for C6 sugars (low) | 3.23 (0.16) |
| Total capital investment | 722 MUSD | 939 MUSD (+30%) | 3.60 (+0.53) |
| | | 505 MUSD (-30%) | 2.54 (-0.53) |
| Discount rate used in MESP calculation | 10 % | 20 % | 4.30 (+1.23) |

As can be seen in Table 7, the MESP was very sensitive to changes in investment costs. Decreasing the total capital investment by 30% decreased the MESP by 0.53

USD/gal, illustrating that decreases in capital costs could improve the economics of the process considerably. In the base case scenario the plant was assumed to be a greenfield project with no existing infrastructure or utility systems. Integrating the plant into an existing industrial facility could be a way to decrease the investment costs considerably, for example by making investments in the boiler and turbine units and wastewater treatment unnecessary. Smaller capital savings could be gained by omitting the investment in acetic acid recovery, which was found to have a relatively long payback period.

Similarly to the absolute level of investment, also the required rate of return on the invested capital (discount rate) had a considerable effect on the MESP. Doubling the discount rate from 10% to 20% increased the MESP by 1.23 USD/gal. Taking into account the risk associated with novel technology and a novel product (organosolv lignin) that have not been demonstrated in large scale, the discount rate might need to be higher than 10%.

Also, changes in the studied technical parameters had an effect on the MESP, with changes in the MESP being in the range of -0.19 to 0.30 USD/gal. The conversion rate both in hydrolysis and fermentation had a relatively considerable effect on the MESP, demonstrating the importance of the overall conversion rate from carbohydrates to ethanol on the economics of the process.

As discussed in the *Introduction*, one of the main arguments for an organosolv pretreatment of lignocellulosic biomass prior to enzymatic hydrolysis is that a relatively pure lignin fraction can be produced. As seen in Tables 5 and 6, with an assumed base case lignin price of 450 USD/MT, the lignin sales are a significant source of revenue and, consequently, a major contributor in the MESP.

The effect of lignin sales on the overall economics of the organosolv process depends considerably on the assumed lignin price. Some price estimates have been presented in the literature (Baker 2010; Pye 2010a; Gosselink 2011; Rushton 2012; van der Linden *et al.* 2012). As there is however no existing commercial, larger scale production of organosolv lignin, the estimates presented in the literature have to be considered as only indicative. The base case lignin price was set in this study at the lower end of the price range presented in the literature. In addition to literature estimates, some indication of the price level could be found from the possible end-products produced from the lignin.

A wide scale of potential application areas have been identified for lignins in general. Holladay *et al.* (2007) classified the various uses into three categories: power-fuel-gasification (utilizing lignin as a carbon source in energy applications such as heat and power and synthesis gas derived fuels), macromolecules (utilizing lignin's macromolecular nature for example in carbon fibers, adhesives, and resins), and aromatic chemicals (breaking up lignin's macromolecular structure to aromatic monomers, including BTX chemicals, (benzene, toluene, xylene) and phenol). Ragauskas *et al.* (2014) reviewed challenges and recent advancements in the processing and use of lignin in materials (carbon fibers, plastics, and composites) and fuels and chemicals. Gosselink (2011) ranked lignin applications based on their value and market volume, from very high-volume, low-value applications (such as energy and fuels) to medium-scale, higher-valued applications (such as aromatic chemicals and phenolic resin) and further to very low-volume, very high-value applications (carbon fibers, fine chemicals). End-product prices ranging from a few hundred dollars per ton and below for energy applications to several thousands for vanillin and phenol derivatives (Gosselink 2011) illustrate the wide price range that could be adopted also for the organosolv lignin.

For organosolv lignins, uses especially in various resin systems such as phenolic and epoxy resins and polyurethanes have been suggested (Pye 2010b; CIMV 2013b). Within these resin systems, applications demonstrated either in pilot or larger scale include the partial replacement of phenol-formaldehyde resin as well as methylene diphenyl diisocyanate (used in polyurethane manufacture) by organosolv lignin in wood products (oriented strand board and medium-density fiberboard), partial replacement of phenol-formaldehyde resin in friction binders and rigid foam insulation, and the partial replacement of epoxy resins in coatings (Rushton 2012). These resins are relatively high-valued products, with the July 2014 prices being approximately 1800 USD/MT for phenolic, 2300 USD/MT for epoxy, and 2500 USD/MT for polyurethane resins (Plastics News 2014). The market volumes of phenolic and polyurethane resins in turn are large with above 10 million MT (MarketsandMarkets 2011; Research and Markets 2012), while the epoxy resin markets is somewhat smaller at approximately 2 million MT (Research and Markets 2013). The larger phenolic and polyurethane markets specifically, both of which are expected to grow in the near term future (MarketsandMarkets 2011; Research and Markets 2012), could be assumed large enough to absorb the amounts of lignin produced in the studied organosolv process (109,000 MT/year) with no major negative effect on the resin prices.

To study the effect of lignin price on the MESP further, the lignin price was varied within a price range. The minimum price of lignin can be considered to be its value as a fuel. As a very conservative fuel pricing scenario, the price of lignin can be calculated from the price of coal. Taking into account differences in the heating values (approximately 25 MJ/kg for lignin and 29 MJ/kg for coal), a coal price of 62.0 USD/MT (U.S. Energy Information Administration 2013c) converts to a lignin fuel value of approximately 53 USD/MT. More favorable fuel price references for lignin would be pellets and forest residues. The maximum price of lignin in the sensitivity analysis was set based on its use in phenolic resins. This use was highlighted by Stewart (2008), who argued that the application of lignin as a substitute for phenol in phenolic resins is a credible option due to the large and growing size of the phenol market and legislative reasons. In phenolic resins lignin can act both as a direct replacement of the resin itself (when lignin is blended with the resin) or as a replacement of the phenol chemical (when lignin is used as a phenolic component in the manufacture of the resin) (Pye 2010a). In this sensitivity analysis the reference product was assumed to be the phenol chemical. Although using organosolv lignin as a substitute for phenol would not directly mean that lignin would be sold for the same price as phenol, not least because modification may be required to enhance the reactivity of the lignin (Stewart 2008; Gosselink 2011), the price of phenol was used here as the optimistic, upper end of the price range used in the sensitivity analysis. In February 2013 phenol sold for approximately 1500 USD/MT (Dietrich 2013). Although higher-value uses than phenolic resins could be found, the average sales price of larger scale lignin production as outlined in this study was assumed to fall within the price range presented above.

Figure 2 shows the results of this analysis. The lignin prices corresponding to the indexed and feedstock cost adjusted MESP of the NREL process (Humbird *et al.* 2011) and the December 2013 market price (Chicago Mercantile Exchange 2013) are presented in the figure. In addition to the effect of lignin price on the base case MESP, also the effects of feedstock and enzyme costs are presented in the figure.

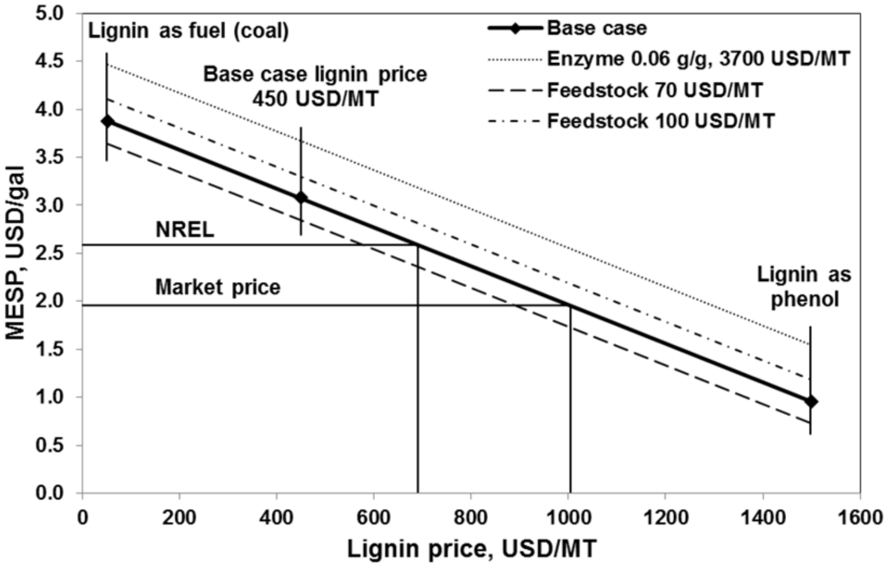

**Fig. 2.** The effect of lignin selling price on the MESP. Market price in the figure refers to the December 2013 market price of ethanol (Chicago Mercantile Exchange 2013) and NREL to the MESP of the NREL study (Humbird *et al.* 2011), indexed to 2013 and feedstock cost adjusted. The figure also presents the effect of enzyme and feedstock costs on the MESP.

It is apparent from Fig. 2 that under a very optimistic scenario with lignin sold at the 2013 phenol price, the MESP would be slightly below 1.0 USD/gal, making the process very attractive. Under the most pessimistic scenario, with lignin priced at its fuel value (with coal as the very conservative price reference), the MESP would be approximately 3.9 USD/gal, considerably higher than the MESP of the NREL dilute acid process (Humbird *et al.* 2011), with feedstock cost aligned with the current study and other costs indexed to 2013 as well as the December 2013 market price of ethanol (Chicago Mercantile Exchange 2013). This result, unsurprisingly, indicates that unless higher-valued applications than combustion can be found for lignin, the organosolv process is not competitive with the NREL dilute acid pretreatment process (Humbird *et al.* 2011) nor could it be used to produce ethanol profitably at the market price (not taking into account any policy instruments to support lignocellulosic ethanol). The lignin prices corresponding to the MESP of the NREL dilute acid process and December 2013 market price are 690 USD/MT and 1000 USD/MT, respectively. The lignin price of 1000 USD/MT is close to the prices assumed by Baker (2010) (below 1100 USD/MT) and van der Linden *et al.* (2012) (975 USD/MT). These higher prices could be realizable if, for example, part of the produced lignin could be sold as a phenol substitute.

In addition to presenting the effect lignin price on the base case MESP, Fig. 2 also presents the effect of variations in feedstock and enzyme costs on the base case MESP. Feedstock and enzyme made a major contribution to the MESP (Table 6). This also resulted in a relatively high sensitivity of the MESP to variations in these cost items. Changing the feedstock price from the base case value of 85 USD/dry MT by 15

USD/dry MT (70 or 100 USD/dry MT) changed the MESP by 0.23 USD/gal. Changing the enzyme loading and price from the base case values of 0.02 g enzyme/g cellulose and 5270 USD/MT to a more conservative 0.06 g enzyme/g cellulose and 3700 USD/MT (Novozymes 2011) increased the MESP by 0.59 USD/gal.

In commercializing the organosolv process, the sensitivity of the MESP to changes in the lignin price presented in Fig. 2 makes a strong case for market creation for the lignin product. The figure also demonstrates the importance of enzyme development and securing of a low-cost feedstock on the viability of this or any other enzymatic bioethanol production process.

## CONCLUSIONS

1. In the previous study (Kautto *et al.* 2013), the organosolv process was found to have higher energy consumption and lower ethanol yield than the dilute acid process due to the recovery of solvent and lower carbohydrate recovery in pretreatment. In the current study, the increased number of processing steps was further found to increase the investment cost.
2. A major advantage of the organosolv process is that it enables the production of a relatively pure organosolv lignin fraction. Also other co-products, namely furfural and acetic acid can be produced. A larger fraction of the incoming raw material is therefore converted to products than in the dilute acid process.
3. The price of lignin defines to a considerable degree whether the revenue from the recovery of the co-products offsets the decreased ethanol yield, poorer energy economy, and higher investment cost. As there is no commercial scale production of organosolv lignin, estimating its possible market price is difficult.
4. A wide range of possible lignin prices was therefore studied in sensitivity analyses. At a base case lignin price of 450 USD/MT, the MESP of the organosolv process was found to be 3.1 USD/gal, being higher than that of the dilute acid process, which was used as a reference.
5. A lignin price of 690 USD/MT was required to make the ethanol production of the organosolv process cost competitive with that of the dilute acid process, illustrating the importance of finding higher value markets for lignin to make the organosolv process competitive.

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## APPENDIX: SUPPLEMENTARY MATERIAL

**Supplementary Table 1.** Equipment Sizing and Costs (EC Refers to Equipment Cost, IF to Installation Factor, IC to Installed Cost, CB to Costing Basis, SE to Scaling Exponent, [1] to Industry Estimate, [2] to Aspen Process Economic Analyzer (AspenTech 2011), [3] to Humbird *et al.* (2011), [4] to Aden *et al.* (2002)). All Costs in MUSD. The Names of the Pieces of Equipment Refer to the Names Used in the Process Flowsheets Presented in the Technical Analysis of the Process (Kautto *et al.* 2013)

| Name | Material | Qty | Size | EC | IF | IC | CB | SE | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| **Feed handling** | | | | | | **41.7** | [1] | | |
| **Pretreatment and lignin recovery** | | | | | | | | | |
| Digester & washing | | | | | | 73.8 | [1] | | |
| Flash tank I | SS316 | 1 | D 2.6 m, h 2.6 m, V 41.0 $m^3$ | 0.4 | 2.0 | 0.9 | [2] | | 5 min liquid hold-up |
| Flash tank II | SS316 | 1 | D 2.4 m, h 7.5 m, V 34.9 $m^3$ | 0.1 | 2.0 | 0.3 | [2] | | 5 min liquid hold-up |
| Flash tank III | SS316 | 1 | D 2.4 m, h 7.2 m, V 33.5 $m^3$ | 0.1 | 2.0 | 0.2 | [2] | | 5 min liquid hold-up |
| Post-hydrolysis reactor | SS316 | 1 | D 5.5 m, h 16.6 m, V 393 $m^3$ | 1.2 | 2.0 | 2.4 | [2] | | Costed as a vertical tank, residence time 60 min |
| Agitator | SS316 | 1 | | 0.1 | 1.5 | 0.1 | [3] | 0.5 | |
| Dilution & mixing tank | SS316 | 1 | D 4.0 m, h 13.7 m, V 169 $m^3$ | 0.6 | 2.0 | 1.2 | [2] | | Costed as an agitated tank, residence time 10 min |
| Lignin filter | SS316 | 1 | | 2.2 | 1.7 | 3.8 | [3] | 0.8 | Pressure filter, scaled based on solids flow |
| Filtration auxiliary equipment | | | | 0.6 | 1.5-3.1 | 1.3 | [3] | 0.5-0.8 | Pumps, tanks, compressors, agitator, cake screw & conveyor |
| Lignin spray dryer | CS | 2 | | 1.3 | 1.7 | 2.3 | [2] | | |
| Screen | SS | 1 | | 0.7 | 1.7 | 1.2 | [2] | | Costed as a screen and dewatering unit |
| Heat exchanger I | SS316;SS | 1 | Area 170 $m^2$ | 0.1 | 2.2 | 0.1 | [2] | | Shell and tube (S&T), overdesign factor (OF) 1.15 |
| Heat exchanger II | SS316;SS | 1 | Area 80 $m^2$ | 0.0 | 2.2 | 0.1 | [2] | | S&T, OF 1.15 |
| Heat exchanger III | SS304;SS316 | 1 | Area 530 $m^2$ | 0.2 | 2.2 | 0.4 | [2] | | S&T, OF 1.15 |
| Pumps | | 7 | | | | 0.4 | | | OF 1.10 |
| **Total process area** | | | | | | **88.5** | | | |

| Name | Material | Qty | Size | EC | IF | IC | CB | SE | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| **Solvent and furfural recovery** | | | | | | | | | |
| Recovery column I | | | | | | | | | |
| Tower | SS316 | 1 | D 5.5 m, h 25.0 m, actual number of trays 35 | 2.2 | 2.4 | 5.3 | [2] | | Tray efficiency 70% |
| Condenser | SS316; SS316 | 1 | Area 3900 m$^2$ | 1.8 | 2.4 | 4.4 | [2] | | |
| Reboiler | SS316; SS316 | 1 | Area 1910 m$^2$ | 1.3 | 2.4 | 3.2 | [2] | | |
| Recovery column II | | | | | | | | | |
| Tower | SS316 | 1 | D 8.2 m, h 25.0 m, actual number of trays 35 | 3.8 | 2.4 | 9.1 | [2] | | Tray efficiency 70% |
| Condenser | SS316;CS | 1 | Area 10100 m$^2$ | 2.5 | 2.4 | 6.1 | [2] | | |
| Reboiler | SS316; SS316 | 1 | | | | | [2] | | Condenser of Recovery column I |
| Furfural distillation | | | | | | | | | |
| Tower | SS316 | 1 | D 0.3 m, h 13.4 m, actual number of trays 16 | 0.1 | 2.4 | 0.2 | [2] | | Tray efficiency 70% |
| Reboiler & condenser | SS316;CS | 1 | Condenser 1.5 m$^2$, reboiler 6.1 m$^2$ | 0.1 | 2.4 | 0.2 | [2] | | |
| Decanter I | SS304 | | D 0.9 m, h 2.7 m, V 1.8 m$^3$ | 0.0 | 2.0 | 0.05 | [2] | | Costed as a vertical tank, residence time 5 min |
| Heat exchanger IV | SS304;SS316 | 1 | Area 1250 m$^2$ | 0.5 | 2.2 | 1.1 | [2] | | S&T, OF 1.15 |
| Heat exchanger V | SS316;CS | 1 | Area 10 m$^2$* | 0.0 | 2.2 | 0.05 | [2] | | S&T, OF 1.15 |
| Heat exchanger VI | SS304;CS | 1 | Area 5 m$^2$* | 0.0 | 2.2 | 0.05 | [2] | | S&T, OF 1.15 |
| Heat exchanger VII | SS304;SS316 | 1 | Area 10 m$^2$* | 0.0 | 2.2 | 0.05 | [2] | | S&T, OF 1.15 |
| Heat exchanger VIII | SS316;SS | 1 | Area 850 m$^2$ | 0.3 | 2.2 | 0.6 | [2] | | S&T, OF 1.15 |
| Pumps | | 5 | | | | 0.2 | [2] | | OF 1.1 |
| **Total process area** | | | | | | **30.7** | | | |
| | | | | | | | | | |
| **Conditioning of the hemicellulosic sugar stream** | | | | | | | | | |
| Evaporation | | | | | | | | | |
| Effects | SS304 | 4 | Total area 15600 m$^2$ | 4.3 | 2.1 | 9.1 | [4] | 0.7 | Scaled based on area |
| Auxiliaries | SS304 | | | 0.8 | | 1.9 | [4] | | Pumps, condenser |

| Name | Material | Qty | Size | EC | IF | IC | CB | SE | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Separation of tarry lignin | SS304 | 1 | Decanter 1.5 m, L 6.2 m, V 23.5 m$^3$ | 0.1 |  | 0.2 | [2], [3] | 0.8 | Decanter (costed as a horizontal vessel), screw, conveyor |
| LMW lignin separation |  |  |  |  |  |  |  |  |  |
| Mixers | SS304 | 4 | D 1.7 m, h 1.7 h, V 3.8 m$^3$ | 0.2 | 1.7 | 0.4 | [2] |  | Agitated vessel (5 min) |
| Settlers | SS304 | 4 | D 1.0 m, L 3.9 m, V 2.8 m$^3$ | 0.1 | 1.7 | 0.2 | [2] |  | Horizontal vessel (5 min) |
| Furfural vacuum distillation |  |  |  |  |  |  |  |  |  |
| Tower | SS316 | 1 | D 3.4 m, h 6.7 m, actual number of trays 6 | 0.4 | 2.4 | 1.1 | [2] |  | Tray efficiency 70% |
| Condenser | SS316;CS | 1 | Area 870 m$^2$ | 0.5 | 2.4 | 1.2 | [2] |  |  |
| Reboiler | SS316;CS | 1 | Area 1240 m$^2$ | 0.6 | 2.4 | 1.3 | [2] |  |  |
| Steam stripping | SS316 | 1 | D 2.9 m, h 9.1 m, actual number of trays 9 | 0.4 | 2.4 | 0.9 | [2] |  | Tray efficiency 70% |
| Neutralization | SS304;SS | 1 |  | 0.1 |  | 0.2 | [3] | 0.5-0.7 | Tank, agitator, mixer, scaled on mass flow |
| Decanter II | SS304 | 1 | D 1.5 m, h 4.4 m, V 8.1 m$^3$ | 0.0 | 2.0 | 0.1 | [2] |  | Costed as a vertical tank, residence time 5 min |
| Heat exchanger IX | SS304;CS | 1 | Area 30 m$^2$ | 0.0 | 2.2 | 0.1 | [2] |  | S&T, OF 1.15 |
| Heat exchanger X | SS316;SS316 | 1 | Area 1020 m$^2$ | 0.5 | 2.2 | 1.0 | [2] |  | S&T, OF 1.15 |
| Heat exchanger XI | SS304;CS | 1 | Area 70 m$^2$ | 0.0 | 2.2 | 0.1 | [2] |  | S&T, OF 1.15 |
| Heat exchanger XII | SS316;SS304 | 1 | Area 980 m$^2$ | 0.4 | 2.2 | 0.9 | [2] |  | S&T, OF 1.15 |
| Pumps |  | 4 |  |  |  | 0.1 | [2] |  | OF 1.1 |
| **Total process area** |  |  |  |  |  | **18.7** |  |  |  |
|  |  |  |  |  |  |  |  |  |  |
| **Acetic acid recovery** |  |  |  |  |  |  |  |  |  |
| AA extraction column |  |  |  |  |  |  |  |  |  |
| Mixers | SS316 | 4 | D 3.6 m, h 3,6 m, V 37.1 m$^3$ | 1.0 | 1.7 | 1.7 | [2] |  | Agitated vessel (5 min) |
| Settlers | SS316 | 4 | D 3.0 m, L 12.1 m, V 86.2 m$^3$ | 0.5 | 1.7 | 0.9 | [2] |  | Horizontal vessel (5 min) |
| AA distillation column I |  |  |  |  |  |  |  |  |  |
| Tower | SS316L | 1 | D 1.4 m, h 6.7 m, actual number of trays 5 | 0.1 | 2.4 | 0.3 | [2] |  | Tray efficiency 70% |
| Reboiler & condenser | SS316L;CS | 1 | Condenser 6 m$^2$, reboiler 180 m$^2$ | 0.1 | 2.4 | 0.1 | [2] |  | Includes a decanter |

| Name | Material | Qty | Size | EC | IF | IC | CB | SE | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| AA distillation column II | | | | | | | | | |
| Tower | SS316L | 1 | D 6.6 m, h 11.6 m, actual number of trays 13 | 1.5 | 2.4 | 3.5 | [2] | | Tray efficiency 70% |
| Reboiler & condenser | SS316L;CS | 1 | Condenser 610 $m^2$, reboiler 180 $m^2$ | 0.4 | 2.4 | 0.9 | [2] | | Includes a decanter |
| AA distillation column III | | | | | | | | | |
| Tower | SS316L | 1 | D 1.2 m, h 46.3 m, actual number of trays 70 | 1.2 | 2.4 | 3.0 | [2] | | Tray efficiency 70% |
| Reboiler & condenser | SS316L;CS | 1 | Condenser 33 $m^2$, reboiler 56 $m^2$ | 0.1 | 2.4 | 0.2 | [2] | | |
| Decanter III | SS304 | 1 | D 0.8 m, h 2.4 m, V 2.4 $m^3$ | 0.0 | 2.0 | 0.1 | [2] | | Costed as a vertical tank (5 min) |
| Heat exchanger XIII | SS316;SS316 | 1 | Area 780 $m^2$ | 0.4 | 2.2 | 0.9 | [2] | | S&T, OF 1.15 |
| Heat exchanger XIV | SS316;SS316 | 1 | Area 10 $m^2$* | 0.0 | 2.2 | 0.1 | [2] | | S&T, OF 1.15 |
| Heat exchanger XV | SS316;SS316 | 1 | Area 20 $m^2$* | 0.0 | 2.2 | 0.1 | [2] | | S&T, OF 1.15 |
| Pumps | | 3 | | | | 0.2 | [2] | | OF 1.1 |
| **Total process area** | | | | | | **11.9** | | | |
| | | | | | | | | | |
| **Enzymatic hydrolysis and fermentation** | | | | | | | | | |
| Enzyme-hydrolyzate mixer | SS316 | 1 | | | | 0.2 | [3] | 0.5 | Scaled on the hydrolyzate mass flow |
| Hydrolysis tanks | SS304 | | | | | 6.4 | [3] | 0.7 | Same scaling basis as above |
| Ethanol fermentation tanks | | | | | | 15.1 | [3] | 0.7 | Scaled on beer flow leaving fermentation, includes coolers and agitators |
| Beer storage tank | SS316 | 1 | | | | 1.2 | [3] | 0.5-0.7 | Scaled on beer leaving beer tank, includes an agitator |
| Seed fermentation tanks | SS304 | | | | | 3.5 | [3] | 0.5-0.7 | Scaled on inoculum flow, includes coils and agitators. |
| Seed hold tank | SS316 | 1 | | | | 0.8 | [3] | 0.5-0.7 | Scaled on inoculum flow, includes an agitator. |
| Heat exchanger XVI | SS;CS | 1 | Area 230 $m^2$ | 0.1 | 2.2 | 0.1 | [2] | | S&T, OF 1.15 |
| Pumps | | 5 | | | | 0.3 | [3] | 0.8 | OF 1.1 |
| **Total process area** | | | | | | **27.7** | | | |

| Name | Material | Qty | Size | EC | IF | IC | CB | SE | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| **Ethanol product and solids recovery** | | | | | | | | | |
| Beer & rectification columns | SS316;CS | 1 | | | | 8.2 | [3] | 0.6 | Includes reboilers, beer column condenser, and feed heat exchanger, scaled on EtOH flow to molecular sieves |
| Water scrubber | SS304;PP | 1 | | | | 0.5 | [3] | 0.6-0.8 | Scaled on the total vents flow, includes a pump |
| Molecular sieve package | SS | 1 | | | | 4.7 | [3] | 0.6 | Scaled on the EtOH product stream |
| Insolubles filter | SS316 | 1 | | | | 3.7 | [3] | 0.8 | Scaled on the insolubles stream |
| Auxiliary equipment | | | | | | 1.3 | [3] | 0.6-0.8 | Auxiliaries include pumps, tanks, compressors, agitator, cake screw, and conveyor, scaled on the insolubles stream |
| **Total process area** | | | | | | **18.4** | | | |
| | | | | | | | | | |
| **Wastewater treatment** | | | | | | **53.5** | [3] | | Not scaled, assumed similar to [3] |
| **Storage** | | | | | | **5.4** | [3] | | Not scaled, similar to [3] |
| **Boiler and turbine** | | | | | | **82.3** | [3] | 0.6 | Scaled on heat load |
| | | | | | | | | | |
| **Utilities** | | | | | | | | | |
| Cooling tower system | | | | | | 3.4 | [3] | 0.6 | Scaled on cooling duty |
| Chilled water package | | | | | | 1.8 | [3] | 0.6 | Scaled on cooling duty |
| Plant/instrument air | | | | | | 0.1 | [3] | | Not scaled, similar to [3] |
| Process water system | | | | | | 0.6 | [3] | | Not scaled, similar to [3] |
| Sterile water & CIP/CS systems | | | | | | 1.4 | [3] | | Not scaled, similar to [3] |
| **Total process area** | | | | | | **7.3** | | | |
| | | | | | | | | | |
| **Total installed equipment cost** | | | | | | **386** | | | |

*****Small heat exchangers that could possibly be omitted

**Supplementary Table 2.** Variable Operating Costs and Revenues from By-products

| | MT/hr | Price, USD/MT | Source of the price | Cash flow, MUSD/a | Remarks |
|---|---|---|---|---|---|
| **Variable costs** | | | | | |
| Feedstock (as dry) | 98.0 | 85 | Berguson *et al.* 2010 | 70.1 | Debarked hardwood 83.3 MT/hr, bark and losses 14.7 MT/hr |
| Chemicals | | | | | |
| Cellulase | 0.6 | 5270 | Novozymes 2011 | 28.7 | |
| Sulfuric acid | 0.8 | 130 | Humbird *et al.* 2011 | 0.9 | |
| Ammonia | 0.5 | 590 | Humbird *et al.* 2011 | 2.6 | |
| Corn steep liquor | 1.1 | 75 | Humbird *et al.* 2011 | 0.7 | |
| Diammonium phosphate | 0.1 | 1300 | Humbird *et al.* 2011 | 1.5 | |
| Sorbitol | 0.03 | 1490 | Humbird *et al.* 2011 | 0.4 | Scaled based on flow to the seed train (Humbird *et al.* 2011) |
| Caustic | 1.1 | 200 | Humbird *et al.* 2011 | 1.9 | Scaled based on ammonia usage (Humbird *et al.* 2011) |
| Flue gas desulfurization lime | 0.4 | 270 | Humbird *et al.* 2011 | 0.9 | Scaled based on sulfuric acid usage (Humbird *et al.* 2011) |
| Cooling tower chemicals | 0.002 | 4040 | Humbird *et al.* 2011 | 0.1 | Usage assumed similar to Humbird *et al.* (2011) |
| Make-up water | 147.1 | 0.22 | Humbird *et al.* 2011 | 0.3 | |
| Kerosene | 0.005 | 1090 | Dennis *et al.* 2013 | 0.05 | |
| Total chemicals | | | | 37.9 | |
| Ash disposal | 2.6 | 36 | Humbird *et al.* 2011 | 0.8 | |
| Natural gas | 2.3 | 4.17 (USD/GJ) | | 4.1 | Source U.S. Energy Information Administration 2013a |
| **Total variable costs** | | | | **112.9** | |
| | | | | | |
| **Revenues from by-products** | | | | | |
| Organosolv lignin | 12.9 | 450 | Estimate | 49.0 | |
| Furfural | 0.3 | 1600 | Arato *et al.* 2005 | 3.7 | Net furfural production, taking the make-up furfural required in the furfural extraction into account |
| Acetic acid | 1.3 | 600 | Kelley 2013 | 6.4 | |
| Electricity | 3.6 (MW) | 52.2 (USD/MWh) | | 1.6 | Source U.S. Energy Information Administration 2013b |
| **Total by-product revenues** | | | | **60.6** | |

**Supplementary Table 3.** Minimum Ethanol Selling Price (MESP) Calculation (in MUSD)

| **Year** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fixed capital investment | 21.9 | 164.3 | 87.6 | | | | | | | | | | | | | | |
| Land | 3.1 | | | | | | | | | | | | | | | | |
| Working capital | | | 34.2 | | | | | | | | | | | | | | |
| Loan payment | | | | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | 61.2 | | | | |
| Loan interest payment | 2.6 | 22.3 | 32.9 | 32.9 | 30.6 | 28.1 | 25.5 | 22.6 | 19.6 | 16.2 | 12.6 | 8.7 | 4.5 | | | | |
| Loan principal | 32.9 | 279.3 | 410.8 | 382.4 | 351.8 | 318.7 | 283.0 | 244.4 | 202.8 | 157.8 | 109.2 | 56.7 | 0.0 | | | | |
| | | | | | | | | | | | | | | | | | |
| Ethanol sales | | | | 144.8 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 |
| Lignin sales | | | | 42.8 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 |
| Other sales | | | | 10.2 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 |
| **Total sales** | | | | **197.9** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** |
| | | | | | | | | | | | | | | | | | |
| Annual manufacturing costs | | | | | | | | | | | | | | | | | |
| Feedstock | | | | 61.3 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 |
| Cellulase | | | | 26.9 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 |
| Natural gas | | | | 3.8 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 |
| Baghouse bags | | | | 0.7 | | | | | 0.7 | | | | | 0.7 | | | |
| Other variable costs | | | | 9.4 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Fixed costs | | | | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 |
| **Total product costs** | | | | **119.2** | **130.0** | **130.0** | **130.0** | **130.0** | **130.6** | **130.0** | **130.0** | **130.0** | **130.0** | **130.6** | **130.0** | **130.0** | **130.0** |
| | | | | | | | | | | | | | | | | | |
| Annual depreciation | | | | | | | | | | | | | | | | | |
| General plant | | | | | | | | | | | | | | | | | |
| DDB | | | | 172.1 | 122.9 | 87.8 | 62.7 | 44.8 | 29.9 | 14.9 | | | | | | | |
| SL | | | | 86.0 | 71.7 | 61.5 | 54.9 | 52.3 | 52.3 | 52.3 | | | | | | | |
| Remaining value | | | | 602.3 | 430.2 | 307.3 | 219.5 | 156.8 | 104.5 | 52.3 | | | | | | | |
| **Actual** | | | | **172.1** | **122.9** | **87.8** | **62.7** | **52.3** | **52.3** | **52.3** | | | | | | | |
| Steam plant | | | | | | | | | | | | | | | | | |
| DDB | | | | 6.2 | 5.7 | 5.3 | 4.9 | 4.5 | 4.2 | 3.9 | 3.6 | 3.3 | 3.0 | 2.8 | 2.5 | 2.2 | 1.9 |
| SL | | | | 4.1 | 4.0 | 3.9 | 3.8 | 3.8 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Remaining value | | | | 82.3 | 76.2 | 70.5 | 65.2 | 60.3 | 55.8 | 51.6 | 47.7 | 44.0 | 40.4 | 36.7 | 33.0 | 29.4 | 25.7 |
| **Actual** | | | | **6.2** | **5.7** | **5.3** | **4.9** | **4.5** | **4.2** | **3.9** | **3.7** | **3.7** | **3.7** | **3.7** | **3.7** | **3.7** | **3.7** |
| | | | | | | | | | | | | | | | | | |
| Net revenue | | | | -132.5 | -63.1 | -25.1 | 3.1 | 16.7 | 19.5 | 23.8 | 79.9 | 83.8 | 87.9 | 91.8 | 92.5 | 92.5 | 92.5 |
| Losses forward | | | | | -132.5 | -195.5 | -220.6 | -217.5 | -200.8 | -181.3 | -157.5 | -77.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Taxable income | | | | -132.5 | -195.5 | -220.6 | -217.5 | -200.8 | -181.3 | -157.5 | -77.6 | 6.1 | 87.9 | 91.8 | 92.5 | 92.5 | 92.5 |
| Income tax | | | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.1 | 30.8 | 32.1 | 32.4 | 32.4 | 32.4 |
| Annual cash income | | | | 17.4 | 34.9 | 34.9 | 34.9 | 34.9 | 34.3 | 34.9 | 34.9 | 32.8 | 4.2 | 63.4 | 63.8 | 63.8 | 63.8 |
| PV of annual CF | | | | 13.1 | 23.9 | 21.7 | 19.7 | 17.9 | 16.0 | 14.8 | 13.5 | 11.5 | 1.3 | 18.4 | 16.8 | 15.3 | 13.9 |
| Total capital investment + interest | 27.6 | 169.7 | 127.9 | | | | | | | | | | | | | | |

| **Year** | **18** | **19** | **20** | **21** | **22** | **23** | **24** | **25** | **26** | **27** | **28** | **29** | **30** | **31** | **32** | **33** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fixed capital investment | | | | | | | | | | | | | | | | |
| Land | | | | | | | | | | | | | | | | -3.1 |
| Working capital | | | | | | | | | | | | | | | | -34.2 |
| Loan payment | | | | | | | | | | | | | | | | |
| Loan interest payment | | | | | | | | | | | | | | | | |
| Loan principal | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| Ethanol sales | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 | 165.5 |
| Lignin sales | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 | 49.0 |
| Other sales | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 | 11.7 |
| **Total sales** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** | **226.1** |
| | | | | | | | | | | | | | | | | |
| Annual manufacturing costs | | | | | | | | | | | | | | | | |
| Feedstock | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 | 70.1 |
| Cellulase | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 | 28.7 |
| Natural gas | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 | 4.1 |
| Baghouse bags | | 0.7 | | | | | 0.7 | | | | | 0.7 | | | | |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Other variable costs | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Fixed costs | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 |
| **Total product costs** | **130.0** | **130.6** | **130.0** | **130.0** | **130.0** | **130.0** | **130.6** | **130.0** | **130.0** | **130.0** | **130.0** | **130.6** | **130.0** | **130.0** | **130.0** | **130.0** |
| | | | | | | | | | | | | | | | | |
| Annual depreciation | | | | | | | | | | | | | | | | |
| General plant | | | | | | | | | | | | | | | | |
| DDB | | | | | | | | | | | | | | | | |
| SL | | | | | | | | | | | | | | | | |
| Remaining value | | | | | | | | | | | | | | | | |
| **Actual** | | | | | | | | | | | | | | | | |
| Steam plant | | | | | | | | | | | | | | | | |
| DDB | 1.7 | 1.4 | 1.1 | 0.8 | 0.6 | 0.3 | | | | | | | | | | |
| SL | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | | | | | | | | | | |
| Remaining value | 22.0 | 18.4 | 14.7 | 11.0 | 7.3 | 3.7 | | | | | | | | | | |
| **Actual** | **3.7** | **3.7** | **3.7** | **3.7** | **3.7** | **3.7** | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| Net revenue | 92.5 | 91.8 | 92.5 | 92.5 | 92.5 | 92.5 | 95.5 | 96.2 | 96.2 | 96.2 | 96.2 | 95.5 | 96.2 | 96.2 | 96.2 | 96.2 |
| Losses forward | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Taxable income | 92.5 | 91.8 | 92.5 | 92.5 | 92.5 | 92.5 | 95.5 | 96.2 | 96.2 | 96.2 | 96.2 | 95.5 | 96.2 | 96.2 | 96.2 | 96.2 |
| Income tax | 32.4 | 32.1 | 32.4 | 32.4 | 32.4 | 32.4 | 33.4 | 33.7 | 33.7 | 33.7 | 33.7 | 33.4 | 33.7 | 33.7 | 33.7 | 33.7 |
| Annual cash income | 63.8 | 63.4 | 63.8 | 63.8 | 63.8 | 63.8 | 62.1 | 62.5 | 62.5 | 62.5 | 62.5 | 62.1 | 62.5 | 62.5 | 62.5 | 62.5 |
| PV of annual CF | 12.6 | 11.4 | 10.4 | 9.5 | 8.6 | 7.8 | 6.9 | 6.3 | 5.8 | 5.2 | 4.8 | 4.3 | 3.9 | 3.6 | 3.3 | 3.0 |
| Total capital investment + interest | | | | | | | | | | | | | | | | |

Discount rate 10%, interest on loan 8%, payback period for loan 10 years, income tax 35%, net present value (of annual CF) 0.0, MESP 3.07 USD/ga

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