Hydrothermal Biomass Conversion as the Enabler of Sustainable Biorefinery

Karhan Özdenkçi
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Abstract

The objectives of this dissertation are to determine the role of biomass conversion processes in sustainable biorefinery and to develop a hydrothermal conversion process as the enabler of sustainable process. The societal and environmental aspects direct the biomass conversion towards 2nd generation. The criteria of sustainable biorefinery include fossil-independent production without compromising the food and animal feed, and flexibility to adapt the changes in market demand and feedstock availability. These criteria can be achieved with multi-product-multi-feed, flexible conversion processes efficient for the high-moisture biomass. Biomass conversion processes are the heart of supply chain networks, influencing the economic and environmental performance and the structure of the whole chain. The conversion processes are to be selected and improved in accordance with the target products and biomass feedstocks.

Hydrothermal processes are suitable for biomass conversion regarding the high moisture and flexibility. It was concluded through a preliminary evaluation that partial wet oxidation can be an intermediate operation of an advanced hydrothermal process, rather than chemical production. Consequently, the experiments included supercritical water gasification of black liquor and partial wet oxidation of saw dust. The dissertation included also feasibility analysis of integrating supercritical water gasification of Kraft black liquor to a pulp mill. Compiling the results, the dissertation proposes a new hydrothermal process for the production of lignin, syngas and bio-oil from the lignocellulosic wastes of various sectors. The proposed conversion process enhances the economic and environmental performance of the involved biomass sectors by valorizing wastes and by-products. This enables sectoral integration network as the supply chain structure.

The sectoral integration network involves pre-treatment of wastes in biomass sites, regional conversion processes and centralized upgrading plants. The advantages of this network includes additional revenue via utilizing wastes of various sectors, distributed financial benefits involving rural areas as well, and reduced financial risks through multiple value creation and adapting the changes in market demand and feedstock availability.

Keywords

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List of abbreviations and symbols

BL: black liquor
CEPCI: chemical engineering plant cost index
CHP: combined heat and power
COD: chemical oxygen demand, g/L
GC: gas chromatography
\( G_{\text{meas}} \): Gibbs free energy calculated with measured activity coefficients
\( G_{\text{calc.}} \): Gibbs free energy calculated with predicted activity coefficients
HTL: hydrothermal liquefaction
HPLC: high pressure liquid chromatography
IRR: internal rate of return
\( K_a \): equilibrium constant of acid dissociation
KBL: Kraft black liquor
\( K_{sp} \): equilibrium constant of salt dissolution
m: molality, mole/kg water
MS: mass spectrometry
NPV: net present value
\( \text{OF}_i \): objective function for fitting the activity coefficient model parameters
\( \text{OF}_{CP} \): objective function for fitting temperature dependence of standard-state specific heat of ions
PSA: pressure swing adsorption
PWO: partial wet oxidation
SCW: supercritical water
SCWG: supercritical water gasification
TOC: total organic carbon, g/L
$\gamma_{w,\text{meas.}}$: measured activity coefficient of water

$\gamma_{w,\text{calc.}}$: predicted activity coefficient of water

$\Delta G^o_{r, \text{meas.}}$: standard Gibbs free energy of reaction calculated with measured saturation data

$\Delta G^o_{r, \text{calc.}}$: standard Gibbs free energy of reaction calculated with temperature-dependent standard chemical potential, including standard specific heat of ions

$c_{p_i}^o$: standard specific heat of component $i$

$\mu_i^o$: standard-state chemical potential of component $i$
This doctoral dissertation consists of a summary of the following publications, which are referred to in the text by their numerals.


Authors’ contribution

**Paper I:** Recovery of sodium organic salts from partially wet oxidized black liquor

Özdenkci formulated the preliminary equilibrium models and performed the chemical speciation calculations. Özdenkci wrote the manuscript as well. Sarwar and Koskinen contributed to the recovery process concepts and related discussion as well as giving comments to the article as whole.

**Paper II:** Gibbs Free-Energy-Based Objective Function for Electrolyte Activity Coefficient Models

Özdenkçi constructed the models and tested the proposed objective functions with the literature data. Özdenkçi wrote the manuscript as well. Koskinen and Sarwar contributed to the importance and applicability of the proposed methodology. Oinas and Sarwar contributed to the validation of the methodology.

**Paper III:** A Study on supercritical water gasification of black liquor conducted in stainless steel and nickel-chromium-molybdenum reactors

Westerlund, Koskinen, De Blasio, Järvinen, Santarelli and Özdenkci planned the study. Westerlund provided the equipment. Lundqvist contributed to the maintenance and installation of the equipment as well as materials and methods section in the article. Lucca and De Blasio performed the supercritical water gasification experiments. Lucca also processed the raw data and provided the resulting plots on gas yields. Özdenkci provided MS and HPLC analysis on the liquid samples and interpreted MS results together with De Blasio. In addition, Özdenkci interpreted the results to determine the impacts of process conditions on the product and on the reaction mechanism. Mulas provided total organic carbon and nitrogen analysis. De Blasio and Özdenkci wrote the
manuscript. Koskinen contributed to the discussions on reaction mechanism, operational issues and conclusion.

**Paper IV:** Techno-economic feasibility of supercritical water gasification of black liquor

Özdenkçi formulated the integration scenarios to a pulp mill and developed the simulation models. Afterwards, Özdenkçi took the main role in equipment design, feasibility calculations and writing the manuscript. De Blasio provided the black liquor analysis and product yields. Sarwar contributed to equipment design, feasibility calculations and clarity of the text. Koskinen and Melin contributed to the content of future aspects and implementation as well as contributing the clarity of the text. Alopaeus contributed to the process simulations and the selection of unit operation conditions as well as contributing the clarity of the text.

**Paper V:** Hydrothermal liquefaction of softwood: selective chemical production under oxidative conditions

Muddassar and Melin performed the experiments and provided product analysis on pH, carboxylic acids, total organic carbon and chemical oxygen demand. Sipponen provided the analysis of sugars, phenolics and ethyl acetate-soluble compounds. Özdenkçì contributed to the product analysis plan, processing the raw data and interpreting the results. Sarwar contributed in the discussions on industrial relevance of the results and clarity on the text. Oinas contributed in the discussions from the practical viewpoints and clarity of the text. Sipponen had the major role in writing the manuscript and in the submission process.

**Paper VI:** A Novel Biorefinery Integration Concept for Lignocellulosic Biomass

Özdenkçi reviewed the literature regarding the supply chain network of biomass and biomass conversion processes. Then, Özdenkçi proposed a new network structure and a hydrothermal conversion process in accordance with the needed features of a sustainable biorefinery. De Blasio and Melin contributed to the discussion about supercritical water gasification. Raja and Melin contributed to the discussion on partial wet oxidation. Koskinen and Sarwar contributed to the proposed conversion process and the discussion on its benefits. Oinas contributed to the clarity of the text. Özdenkçi wrote the manuscript and handled the submission.
1. Introduction

The critical sustainability issues currently involve environmental impacts associated with carbon emissions and other pollutants, e.g. climate change, water and air pollution, large land usage for solid wastes, release of toxic gases in landfills, and stratospheric ozone depletion. In addition, depletion of fossil resources introduce another sustainability problem since fossils compose currently the main source used in refinery sectors and energy production. Therefore, the further developments should address the resource depletion and waste dispositions.

The sustainability issues has driven the industrial ecology from linear to circular economy model. Figure 1 illustrates the linear economy with waste management and circular economy models. The linear model steps include the extraction of raw materials from nature, production of the desired products and disposal of the product after usage. The wastes occurring at the production step are also treated and discharged to the nature. Despite improving the situation, the integration of waste management systems does not sufficiently address the sustainability issues either. The continuous increase in disposal amounts causes further issues of sufficiency of capacity, sorting the disposals precisely and transportation costs. Furthermore, depletion of natural resources makes the raw material extraction step increasingly more difficult. In contrast, circular economy involves approaching to wastes as the raw materials of some other production, e.g. the recovery of valuable components from the disposed products, chemical and energy recovery from the production wastes and regenerating the resources in case of biomass (Ellen MacArthur Foundation, 2015). This model provides the benefits of reduced emissions and increased resource yields through waste utilization and multiple value creation mechanisms (Ellen MacArthur Foundation, 2015). Some
examples of industrial applications include solid recovered fuels from disposals, heavy metals and minerals recovery from disposed products and waste streams, and energy or fertilizer from manure in livestock as well as integrated processes sharing infrastructure.

Figure 1. Linear economy model with waste management (top) versus circular economy model (bottom) (Özdenkçi and Sarwar, 2017)

Referring to the depletion and environmental impacts of fossils, biomass has increasingly become an important raw material as a renewable source especially for refinery and energy sectors (Cherubini, 2010). Biomass is already involved in various sectors such as agriculture, livestock, forestry,
pulp and paper, textile and aquaculture. From the circular economy viewpoint, all these sectors are interconnected through waste and/or by-product of a sector being useful raw material for chemical production in another sector or energy production. For instance, agricultural residues can be processed to produce energy or chemicals. Similarly, pulp and paper industry uses wood as the raw material, and the by-products (black liquor and bark) is utilized as the energy source. The chemicals produced from lignocellulosic biomass include phenol and phenol derivatives through lignin, and sugars and alcohols through cellulose and hemicellulose as well as other various organics (Kohli et al., 2019). Manure from livestock and aquaculture can be used as raw material of fertilizers or energy. In addition, the recycled papers and textile products can also be raw material for paper, textile or energy production. Furthermore, the carbon dioxide emission from energy production can be utilized for algae production and acidification operations. Algae can be used in various applications, such as for energy, fertilizer and pigments. Lipid fraction of algae is a raw material for biodiesel production (Luque et al., 2008). Meanwhile, protein and carbohydrate fractions can be used to produce food and animal feed as well as industrial chemicals or biofuels (Elliott, 2004; Kohli et al., 2019). To sum up, biomass as a renewable source is a potential tool for sustainable development and circular economy.

The future target of biorefinery would be sustainable production of chemicals, fuels and energy from biomass without the need of fossil fuels. As a typical approach, co-processing biomass with fossil-based fuel can only be a short- or middle-term solution, benefiting to use the existing infrastructure during the transition state (Yue et al., 2014). Referring to the interconnections of biomass sectors, the current investigations have been directed towards the whole supply-chain network of biomass-to-products: harvesting biomass in fields, transporting to conversion plants, chemical conversion of biomass to products and finally transport of the products to the demand sites (Sharma et al., 2013). Among these steps in a supply chain, the chemical conversion of biomass is the heart of the network: introducing the most influence to the configuration of a supply-chain and performance in terms of sustainability elements (profitability, environmental impacts and societal aspects). Consequently, the development of biorefinery concept involves two main subjects: chemical conversion of biomass and the supply-chain network optimization.
1.1 Supply-chain network and sustainable biorefinery

Biomass feedstock is classified into two categories as 1st generation referring to dedicated edible crops and 2nd generation referring to non-edible crops and waste/side streams (Luque et al., 2008). This influences the selection of conversion processes as well. 1st generation biomass is close-to-uniform feedstock, thus processed with inexpensive and simple conversion processes (Cherubini, 2010; Elliott, 2004). The most typical examples include biodiesel production from vegetable oils and bioethanol production from energy crops (such as sugar cane, corn and wheat). However, 1st generation biomass processing compromises the needs food and animal feed sectors in water and land usage. Therefore, this type of processing might cause equal or even more carbon emissions than fossil-based production, counting also the plant growth steps of harvesting, machinery, fertilizers and distribution (Luque et al., 2008). Moreover, another issues include the availability of crops only in certain seasons and spontaneous degradation in case of long-term storage. Consequently, it can clearly be stated that the complete replacement of fossils with 1st generation biorefinery is unsustainable. In contrast, 2nd generation biorefinery has potential for sustainable replacement of fossils: utilizing non-edible feedstocks (e.g. wood, grass or non-edible crops) and by-products or waste streams (e.g. black liquor, straw, bark, saw dust). Despite the potential, waste biomass in excess amounts are mostly disposed or used for low-value purposes. This results from the 2nd generation biorefinery involving more advanced processes, thus causing some techno-economic issues. These issues include variety of feedstock, high processing costs and operational concerns of each processing method. This aspect directs the investigations to the supply chain structure and optimizing the whole chain.

The design or optimization of supply chain network refers to the determination of capacities and locations of conversion processes and upgrade/purification plants (Sharma et al., 2013). The network structure can be classified into three main types: centralized, decentralized and distributed-centralized networks, as shown in Figure 2 (Yue et al., 2014). Centralized network refers to transporting waste from all source places to a large-capacity single plant followed by being processed to final products in this single plant. However, despite providing more efficient processing plants, it is usually too costly to transport of waste biomass to a processing...
plant, and some biomass types can degrade spontaneously in case of long-time storage. In contrast, distributed network refers to waste being processed to products at each source site followed by transferring the products to demand sites. However, a fully distributed structure does not introduce the optimum network either due to high transportation costs of products to demand sites and high operation costs of small-capacity plants. To address the issues of these network structures, a proposed network involves distributed hubs for collection and pre-treatment followed by a centralized plant for biomass processing to the desired products (Bowling et al., 2011). It was widely stated that a balanced network provides the optimum production from waste biomass. On the other hand, the centralized network involving collection hubs still introduce high transportation costs as well as long storage time potentially causing deterioration of biomass. These issues are addressed by increasing the energy density of feedstock through an intermediate conversion and transferring the energy-dense intermediates to the conversion plants for final products (Papendiek et al., 2012). This concept introduces the further progress in the structure, referred to as distributed-centralized network, as shown in Figure 2. For instance, the comparisons of centralized and distributed-centralized structures concluded that distributed-centralized structure gives the optimum results on the case studies of pyrolysis followed by gasification and Fischer-Tropsch synthesis (Kim et al., 2011), and a biomass-to-liquid fuel network (You and Wang, 2011). These case studies also concluded that the distributed-centralized network is more robust to the variations in market demand or prices than the centralized network (Kim et al., 2011; You and Wang, 2011). Furthermore, as a social aspect, distributed-centralized approach contributes to the development of rural areas as well by introducing more industrial production facilities and employment close to the rural sites (Papendiek et al., 2012). This would lead to more close-to-uniform the population distribution between rural and urban areas together with the social services, rather than high accumulation in certain industrial regions (Papendiek et al., 2012).
Figure 2. Supply chain network structures (Paper VI)
Referring to the ultimate target of sustainable production, the goal is to improve economic and environmental aspects of biomass sectors in order to enable the replacement of fossil with biomass. The sustainable biorefinery concept should fulfil the criteria listed below:

- no compromise with critical needs, such as food and animal feed
- maintaining the regeneration of biomass and biodiversity
- minimum environmental impacts
- the ability to adapt the variations in quality and quantity of biomass feedstock
- flexible operation to adapt the changes in market demand

However, these features require multi-feed-multi-product, flexible and techno-economically efficient conversion processes within effective supply chain networks. In other words, biomass conversion process is the heart of a biomass supply chain.

### 1.2 Biomass conversion technologies

The conversion processes are classified as thermal, biological and hydrothermal based on the treatment method. The biological processes include the conversion achieved with enzymes or microorganisms, e.g., biogas production from food waste, the hydrolysis of carbohydrates or cellulose and hemicellulose for sugar production, and fermentation of sugars for alcohol production (Ishola et al., 2015). The biological processes can selectively produce the desired products with relatively higher purity. However, these processes have operational issues affecting the flexibility: very long residence time (days), difficult process control and product inhibition. The thermal processes include the conversion with heat treatment and occur at high temperature. The main routes include gasification for syngas production or pyrolysis for crude bio-oil production followed by further processing to biofuels or various chemicals (Balat et al., 2009a, 2009b). Another example is torrefaction to remove water and some volatiles. The thermal processes are suitable for low-moisture feedstock, thus usually requiring the pre-treatment of drying or evaporation for biomass feedstock. On the other hand, these pre-treatments are the main source of exergy loss (Saidur et al., 2012). The hydrothermal processes use water as the reaction media, thus eliminating the energy-consuming drying or evaporation requirement, benefiting from
the changes in water properties with high pressure and temperature (Kruse and Dahmen, 2015). These processes produce the same products with thermal processes. Nevertheless, the hydrothermal processes provide higher yields and product quality as well as occurring at lower temperatures than the thermal processes. Despite the drawback of requiring high pressure, the hydrothermal processes have short residence time; thus being suitable referring to biomass properties, adaptability and flexibility. However, the overview schemes of conversion routes rarely include the hydrothermal processes. The main hydrothermal processes include partial wet oxidation (PWO), supercritical water gasification (SCWG) and hydrothermal liquefaction (HTL).

**Hydrothermal processes**

PWO is an exothermic process occurring in liquid-phase at pressure ensuring the liquid phase operation. Organic content is decomposed to some intermediate compounds in PWO, not complete oxidation to carbon dioxide and water. The PWO studies examined for chemical production, e.g. the impacts of temperature and catalyst on the production of carboxylates from Kraft black liquor and wheat straw black liquor with the residence time of 30 minutes (Muddassar et al., 2015). PWO is also involved in an industrial application of lignin recovery from black liquor: namely LignoForce process, PWO of black liquor prior to acidification to enhance the filtration of lignin and to obtain sulphur-free lignin (Kouisni et al., 2016).

The HTL process aims at bio-oil production as the main product and generates also char and water-soluble organics as by-products. Despite requiring upgrading for usage as fuel, bio-oil produced via HTL contains less oxygen than bio-oil produced via fast pyrolysis; therefore, bio-oil produced via HTL requires less hydrogen when upgrading (Tekin et al., 2014). The current achievement in HTL of lignocellulosic biomass involves 30-40 % of oil yield (by weight on dry basis) with the addition of alkaline (e.g. sodium carbonate) in moderate amounts and at the temperature range of 330-350 ºC, dramatically lower temperature than fast pyrolysis (Toor et al., 2011). Furthermore, the energy recovery is usually around 80 % in HTL processes (Toor et al., 2011). However, a techno-economic analysis showed that HTL of wood biomass is not economically competitive with petroleum-based gasoline (Zhu et al., 2014). Nevertheless, HTL has room for improvements: reducing pre-treatment
cost through wet biomass or wet biomass blended with solid biomass, reducing the feedstock price by using waste biomass rather than wood, and reducing the capital cost through a distributed HTL plant.

SCWG is another hydrothermal process operating at higher temperature and pressure than the critical point of water (374 °C and 22.1 MPa). SCWG produces syngas (mainly composed of carbon dioxide, carbon monoxide, hydrogen and methane with minor amounts of C2 or heavier gases) as the main product and char as the by-product. Many studies investigated SCWG of model compounds representing sugars (Hao et al., 2003; Kabyemela et al., 1999) or lignin (Resende et al., 2008; Wahyudiono et al., 2011) to investigate the reaction phenomena. Due to complicated reaction mechanism not fully understood yet, kinetic modelling has issues of lacking the whole conversion route, using lumped models or insufficient representation of reaction rates and temperature effect (Yakaboylu et al., 2015). Nevertheless, kinetic studies determined that the depolymerisations of cellulose, hemicellulose and lignin to monomers occur very fast under SCW (Sasaki et al., 1998; Yong and Matsumura, 2012). Moreover, SCWG of real biomass can provide data including the interactions of different constituents as well as data for the techno-economic assessment. For instance, carbohydrates act as a hydrogen donor for lignin decomposition in case of a lignocellulosic biomass (Yoshida and Matsumura, 2001). The main process parameters influencing the gas yields include temperature, feed concentration, residence time and catalyst. In contrast, the impact of pressure is minor when operating under 23-29 MPa (Kang et al., 2015; Sricharoenchaikul, 2009). The gas yields increase with temperature and residence time and decrease with feed concentration. The alkali content promotes gasification as homogeneous catalyst, and transition metals also increases the gas yields as heterogeneous catalyst or reactor wall (Guo et al., 2010). However, the process conditions have inter-dependent impact on the reaction phenomena and gas yields. For instance, high temperature and long residence time together causes repolymerization of phenolics, thus reducing the gas yields (Fang et al., 2008). The catalytic impact also depends on temperature. For instance, Inconel reactor promotes the gasification reactions more intensively than stainless steel at high temperature (600 °C or above) whereas stainless steel reactor provides slightly more or similar yields with Inconel reactor at low temperature (400-500 °C) (Castello et al., 2017). From the technology readiness level
viewpoint, SCWG has reached the pilot scale: Verena pilot plant with the capacity of 2.4 tons of wet biomass per day (Boukis et al., 2007), other pilot plant in Hiroshima with the capacity of 1 ton per day (Matsumura, 2015), the pilot plant in Northwest Laboratory with the capacity of 0.6 ton per day, and PSI process with the capacity of 1.2 tons of wet biomass per day (Vogel, 2017). However, commercialization can be achieved after reducing the production costs further and techno-economic assessments for various feedstocks.

**Technology readiness level and criteria of conversion processes**

To sum up, no commercialized technology has been achieved yet converting 2\textsuperscript{nd} generation biomass to fuels and value-added chemicals, despite the presence of pilot- or demo-scale facilities for several technologies. Biological conversion is suitable only for biomass feedstock with high sugar content and for a specific product, not enabling flexibility. Thermal conversion has the issues associated with energy-consuming drying or evaporation steps. Hydrothermal conversion has the issue of high operation cost due to high pressure and relatively dilute reactor inlet. Therefore, further improvements are required to achieve the techno-economic feasible conversion of 2\textsuperscript{nd} generation biomass. Referring to the sustainability criteria of biorefinery and the links between conversion process and the supply chain, a biomass conversion process should have the features below:

- multi-feed-multi-product process
- flexible in terms of switching between the products and adjusting the amounts
- processing wide spectrum of feedstock: from various sectors, in liquid or solid phase
- techno-economically suitable conversion process regarding biomass properties
2. Objectives

The objectives of this research are:

- to develop a hydrothermal biomass conversion process as the enabler of sustainable biorefinery
- to determine the role of biomass conversion in sustainable biorefinery

To reach these objectives, the scientific and engineering aspects include product yields and energy efficiency of the process, the integration concept for an industrial application, the ability to process various biomass feedstocks in liquid and solid phases as well as flexibly producing multiple products.

Figure 3 shows the contributions of involved articles to the overall objectives of this research. Paper I evaluated PWO of black liquor through aqueous electrolyte modeling for carboxylic acid or salt production, pointing the needs for electrolyte modeling and directing the research to another alternative, namely SCWG. Paper II proposed a new methodology for the development of aqueous electrolyte modeling, reducing the amount of data. This can be useful when developing model for multicomponent systems involved in biorefinery processes. Paper III and Paper IV evaluated SCWG of black liquor: techno-economic assessment in Paper IV based on the experimental results presented in Paper III. Paper V investigated the hydrothermal liquefaction of sawdust under oxidative conditions for producing various chemicals including bio-oil, to determine the conversion of solid feedstock. Compiling the findings of the first five papers and the criteria of sustainable biorefinery, Paper VI proposed a new hydrothermal process as well as network structure.
Figure 3. Mapping the papers on the regard of research objectives
3. Materials and Methods

The research includes experiments of SCWG followed by techno-economic evaluation and conceptual progress towards sustainable biorefinery. The experiments include partial wet oxidation (PWO), supercritical water gasification (SCWG) and oxidative hydrothermal liquefaction (HTL) operations. The feedstocks were Kraft black liquor (KBL), wheat straw black liquor (WSBL) and saw dust (SD).

3.1 Aqueous electrolyte modelling

The purpose of Paper I was to quickly evaluate PWO as the conversion process option by investigating the recovery of carboxylates from the downstream. The study used a simplified electrolyte model and water-salt system to obtain the conclusive remarks quickly. The downstream system was simplified to the mixture of water, sodium, formate and acetate based on the yields obtained in PWO studies at 20 bars and 200 °C, ignoring the polymeric or heavier organics and other inorganics: 1.26 m sodium, 0.42 m formate and 0.84 m acetate. As the electrolyte model, Bromley model is used for activity coefficients as a function of temperature and composition (Bromley, 1973). The model equations are shown in Paper I. This model is an empirical model counting the dissolved ions as one complex system. Therefore, this model includes less number of parameters to fit compared to local composition models, and binary water-salt data is sufficient. Paper I gives the equations of Bromley model and the interaction parameters used in this study. Equations 1 and 2 show the dissolution of salts (sodium formate and sodium acetate, respectively), and Equations 3 and 4 show dissociation of acids (formic acid and acetic acid, respectively) together with equilibrium constants:
\[
\text{NaCHOO}_{(s)} \leftrightarrow \text{Na}^+_{(aq)} + \text{CHOO}^-_{(aq)} \quad K_{sp1} = m_{Na^+}m_{\text{CHOO}}\gamma_m^2 \\
\text{NaCH}_3\text{COO}_{(s)} \leftrightarrow \text{Na}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)} \quad K_{sp1} = m_{Na^+}m_{\text{CH}_3\text{COO}}\gamma_m^2 \\
\text{CHOOH}_{(aq)} \leftrightarrow \text{H}^+_{(aq)} + \text{CHOO}^-_{(aq)} \quad K_{a1} = \frac{m_{H^+}m_{\text{CHOO}}\gamma_m^2}{m_{\text{CHOOH}}\gamma_{\text{CHOOH}}} \\
\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow \text{H}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)} \quad K_{a2} = \frac{m_{H^+}m_{\text{CH}_3\text{COO}}\gamma_m^2}{m_{\text{CH}_3\text{COOH}}\gamma_{\text{CH}_3\text{COOH}}} 
\]

where \( m \) represents the molal concentration and \( \gamma_m \) represents the mean molal activity coefficients of ions. The equilibrium constants of reactions were fitted to temperature. Paper I shows the parameters and the comparison of calculated versus measured equilibrium constants. The fitting is quite accurate as shown in Paper I. The mass balances are shown in Equations 5-7.

\[
\text{Sodium: } m_{\text{Na total}} - m_{\text{Na}^+_{(aq)}} - m_{\text{NaFormate}_{(s)}} - m_{\text{NaAcetate}_{(s)}} = 0 \\
\text{Acetate: } m_{\text{Acetate total}} - m_{\text{Acetate}^-_{(aq)}} - m_{\text{HAcetate}_{(aq)}} - m_{\text{NaAcetate}_{(s)}} = 0 \\
\text{Formate: } m_{\text{Formate total}} - m_{\text{Formate}^-_{(aq)}} - m_{\text{HFormate}_{(aq)}} - m_{\text{NaFormate}_{(s)}} = 0
\]

Then, the system was solved through the set of equations combining the mass balances, dissociation constants and activity coefficient models to determine the chemical speciation. The results also include acid and salt recovery with respect to temperature and pH as well as a process diagram of crystallization.

Paper II proposed a new methodology in the development of aqueous electrolyte models: parameter fitting in activity coefficient models and standard-state specific heat of ions. Paper II used Bromley as a simple model and Pitzer model as an advanced one for calculating mean molal activity coefficients. Pitzer model is a local composition-based model (Pitzer, 1973). The equations of this model are given in Paper II. In addition, the data was collected from the literature on activity coefficients from zero to saturation concentration in various temperatures and standard-state specific heat for sodium chloride, potassium chloride and potassium bromide. The range of data and references are listed in Paper II. Then, the methodology proposed in Paper II is constructed based on the two thermodynamic aspects: the equilibrium being defined by minimum
Gibbs free energy rather than activity coefficients and speciation results being sensitive to the errors around the saturation concentrations. The interaction parameters of activity coefficient models were fitted based on Gibbs free energy as shown in Equation 8, instead of squared error of activity coefficient or natural logarithm of activity coefficient. The objective function to be minimized is the squared error of Gibbs free energy obtained with measured and calculated activity coefficients. Then, this objective function becomes a function of temperature and composition. Equation 9 shows the objective function after substituting chemical potentials into Equation 8 while Equation 10 and 11 show the cases of fitting only mean molal activity coefficient or only osmotic coefficient:

\[
OF_Y = \frac{1}{NP} \sum_d^{NP} (G_{\text{meas.}} - G_{\text{calc.}})^2
\]  

\[
OF_Y = \frac{1}{NP} \sum_d^{NP} \left[ m_w (RT\ln \gamma_{w,\text{meas.}} - RT\ln \gamma_{w,\text{calc.}}) + \sum_i^{\text{ions}} m_i (RT\ln \gamma_{i,\text{meas.}}^m - RT\ln \gamma_{i,\text{calc.}}^m) \right]^2
\]  

\[
OF_Y = \frac{1}{NP} \sum_d^{NP} \sum_i^{\text{ions}} (m_i RT\ln \gamma_{i,\text{meas.}}^m - m_i RT\ln \gamma_{i,\text{calc.}}^m)^2
\]  

\[
OF_Y = \frac{1}{NP} \sum_d^{NP} (m_w RT\ln \gamma_{w,\text{meas.},d} - m_w RT\ln \gamma_{w,\text{calc.},d})^2
\]

where \( m_w \) represents the moles of water per kg (equal to 55.51), \( m_i \) represents the molal concentration of the ion \( i \), \( \gamma_{i,\text{meas.}}^m \) represents the mean molal activity coefficient obtained through experimental measurements and \( \gamma_{i,\text{calc.}}^m \) represents the calculated value through an activity coefficient model. Another proposed fitting is to fit the standard-state specific heat of ions based on the saturation data, instead of extrapolating the specific heat measurements of dilute solutions to infinite dilution. The chemical potential of solid salt is equal to that of ions at equilibrium. Therefore, the standard Gibbs free energy of a dissociation reaction can be calculated through temperature-dependent chemical potentials as well as saturation concentration and mean molal activity coefficient. For a salt dissociating as shown in Equation 12, Equation 13 shows the standard Gibbs free energy of reaction with measured molality and activity coefficient at saturation. When the activity coefficient data is available up to some molality less than saturation, Equation 13 can involve the measured saturation molality with estimated activated coefficient.
Equation 14 shows the standard Gibbs free energy of reaction with temperature-dependent standard chemical potential, i.e. including standard specific heats of ions. Equation 15 shows the temperature dependence of chemical potential. Equation 16 shows the temperature dependence of standard-state specific heat of water, of which the parameters are given in DIPPR801 (American Institute of Chemical Engineers, 2005). Equation 17 shows the temperature dependence of standard-state specific heat of ions (Thomsen et al., 1996), of which the parameters are to be fitted through the objective function shown in Equation 18.

\[ C_c A_a(s) \leftrightarrow cC(aq) + aA(aq) \] (12)

\[ \Delta G_r^{o\meas.} = -RT\ln\left(m_c^{o\meas.} m_{A_{\text{aq}}^{o\meas.}} (y^m)^a+c \right) \] (13)

\[ \Delta G_r^{o\text{calc.}} = c\mu_{c_{\text{aq}}^{o\meas.}} + a\mu_{A_{\text{aq}}^{o\meas.}} - \mu_{cA_{a}(s)}^o \] (14)

\[ \mu_i^o = \Delta_f H_i^o(298.15 \, K) + \int_{298.15 \, K}^{T} c_{pi}^{o} \, dT - T \left( \Delta_f S_i^o(298.15 \, K) + \int_{298.15 \, K}^{T} c_{pi}^{o} \, dlnT \right) \] (15)

\[ c_{p_w}^{o} = a_w + b_w T + c_w T^2 + d_w T^3 + e_w T^4 \] (16)

\[ c_{p_i}^{o} = a_i + b_i T + \frac{c_i}{T-200} \] (17)

\[ OF_{cp} = \frac{1}{N_P} \sum_{d}^N \left( \Delta G_r^{o\meas.} - \Delta G_r^{o\text{calc.}} \right)^2 \] (18)

The proposed methodology was evaluated by comparing the accuracy of solubility estimates of this methodology versus temperature with the estimates of the common methodology conducted with the same set of data (interaction parameters fitted with respect to the squared error of natural logarithm of activity coefficients and ionic specific heat parameters fitted with the data of dilute measurements). Since Bromley model is inaccurate in water activity, solubility estimates were obtained by equalizing the equilibrium constants calculated with fitted values of molality and activity coefficient to the equilibrium constants calculated with measured solubility and activity coefficient at saturation. When using Pitzer model, the solubility estimates were obtained by minimizing the total Gibbs free energy of a binary water-salt system with respect to molality.
3.2 Supercritical water gasification of Kraft black liquor

The feedstock for SCWG was received from a pulp mill using hardwood and softwood as the raw material with fractions of 0.3 and 0.7, respectively. The main properties of black liquor is shown in Table 1 as received from the pulp mill. Before the SCWG experiments, the feedstock was diluted by adding distilled water in the amount of 2.85 times of the received black liquor by volume.

Table 1. The main properties of black liquor as received from the pulp mill (Paper III)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low heating value</td>
<td>14.4 MJ/kg dry solid</td>
</tr>
<tr>
<td>Dry solid content</td>
<td>41.7 wt-%</td>
</tr>
<tr>
<td>Ash content</td>
<td>15.2 wt-%</td>
</tr>
<tr>
<td>pH</td>
<td>13.3</td>
</tr>
<tr>
<td>Alkali-soluble lignin</td>
<td>162.6 g/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>34.2 g/L</td>
</tr>
<tr>
<td>Sulphur</td>
<td>15.4 g/L</td>
</tr>
<tr>
<td>Density</td>
<td>1.19 kg/L</td>
</tr>
</tbody>
</table>

The experimental setup is shown in Figure 4. The setup involves feed cyclinders, the tubular reactor, condenser, back pressure valve and sampling line. The start-up operation involved reaching the experimental temperature and pressure by filling the system with deionized water. Pressure was controlled through the back pressure valve and monitored through a pressure meter. The temperature in the reactor was monitored through thermocouples at the beginning, at the middle and at the end of the reactor. The thermocouples were located on the outer surface of the reactor wall, and the reactor was surrounded by insulation material. The reactor involves electrical heating elements for temperature control. During the start-up, the reactor was heated with the heating rate of 0.04 K/s to minimize the thermal stress. After start-up, the biomass was inserted to feed cylinders and fed to the reactor, being pressurized by water pumped on top with high pressure pump. During the biomass conversion, temperature was controlled through electrical heaters, and pressure was controlled through back pressure valve. The product mixture went through condenser after passing through the reactor. Then, the samples were collected in a sampling bag.
Paper III investigated the impacts of temperature and reactor material under a constant pressure and inlet flowrate of 25 MPa and $6 \times 10^{-5}$ L/s. The investigated temperature range was 500-700 °C, and the reactor materials were Inconel 625 (61.4 % Ni, 20.9 % Cr and 8 % Mo by weight as the main components) and stainless steel 316 (69.4 % Fe, 16.5 % Cr, 10.2 % Ni by weight). Paper III gave the complete composition of the reactor materials as well. The reactor volume is 81 mL with the inner diameter of 1.1 cm and outer diameter of 2.5 cm. Since the inlet flowrate is constant, the residence time slightly changed with temperature. Assuming pure supercritical water properties in the reactor, the residence times were calculated as 1.9, 1.5 and 1.3 minutes for operations at 500, 600 and 700 °C, respectively.

The products were analyzed in both gas and liquid phases. The phases were separated from the sampling bags after the bags were kept at room conditions. Then, the gas phase was analyzed with GC-MS for the composition. The amount of gas was calculated from the volume. The gas yields were calculated by using the amount and composition data. The analysis of liquid samples include total organic carbon (TOC), chemical oxygen demand (COD), high performance liquid chromatography (HPLC), nitrogen, and mass spectrometry (MS). HPLC provided the concentrations of light carboxylates (acetate, formate, lactate, and propionate) and alcohols (ethanol, propanol and butanol). MS provided the detection of compounds having molecular weight of 100-400 g/mol.
3.3 Process Simulation and Feasibility Assessment

The integration of SCWG to a pulp mill was evaluated through feasibility assessment. The case is defined as shown in Table 2. The mill capacity is 400 000 tons of air-dried (ADt) pulp per year. Assuming 10 kg of weak black liquor generation per kg of pulp and 20 % of black liquor being processed in SCWG process, the capacity of SCWG process is defined as 100 t/h weak black liquor inlet. Five integration scenarios were defined based on the reactor material and target product as shown in Table 3.

Table 2. The pulp mill case and the integration of SCWG plant

<table>
<thead>
<tr>
<th>The capacity of pulp mill</th>
<th>400 000 ADt / year</th>
</tr>
</thead>
<tbody>
<tr>
<td>The weak BL amount</td>
<td>4 Mton / year</td>
</tr>
<tr>
<td>The fraction of KBL to SCWG plant</td>
<td>20 %</td>
</tr>
<tr>
<td>Annual operation duration</td>
<td>8000 h / year</td>
</tr>
<tr>
<td>The SCWG plant capacity</td>
<td>800 ktons weak BL inlet / year</td>
</tr>
<tr>
<td></td>
<td>100 t weak BL inlet / h</td>
</tr>
</tbody>
</table>

Table 3. The scenarios of SCWG plant integration

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>The target product</th>
<th>The reactor type</th>
<th>Reactor temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHP-Inc-700</td>
<td>CHP</td>
<td>Inconel 625</td>
<td>700 °C</td>
</tr>
<tr>
<td>CHP-SS-700</td>
<td>CHP</td>
<td>Stainless steel 316</td>
<td>700 °C</td>
</tr>
<tr>
<td>H2-Inc-600</td>
<td>Hydrogen</td>
<td>Inconel 625</td>
<td>600 °C</td>
</tr>
<tr>
<td>H2-Inc-700</td>
<td>Hydrogen</td>
<td>Inconel 625</td>
<td>700 °C</td>
</tr>
<tr>
<td>H2-SS-700</td>
<td>Hydrogen</td>
<td>Stainless steel 316</td>
<td>700 °C</td>
</tr>
</tbody>
</table>

The SCWG of black liquor was simulated based on the process conditions and yields obtained in Paper III. The process simulation requires the definition of feedstock, yields and thermodynamic methods as well as unit operations. The feedstock was defined as mixed stream of conventional and non-conventional compounds. Table 4 shows the defined feed stream as weak liquor from the pulping unit at 175 °C and 11 bars. The black liquor in Paper III was more concentrated than typical weak black liquor because of being received after some evaporation steps. Paper IV first made a projection for weak black liquor. In addition, the enthalpy and density methods are defined as “HCOALGEN” (with all optional codes of 1) and “DCOALIGT”, respectively, for the non-conventional compounds. Despite being originally defined for coal, these methods are reasonable for techno-economic assessment in this study since the streams are very dilute. Therefore, the extent of inaccuracy in enthalpy and density of non-conventional compounds does not influence the results significantly. In addition, the yields were converted into the basis of mass per mass non-
inert as shown in Table 5, defining ash as the only inert component. The simulations involved yield reactor with the defined yield data. The thermodynamic method was defined as Soave–Redlich–Kwong (SRK) model. Paper IV gives more details including free-water and water solubility methods.

Table 4. Feed stream composition and flow rates (Paper IV)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mixed Mass flow rate (kg/h)</th>
<th>NC Solid (non-conventional solid) Mass flow rate (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>48</td>
<td>Lignin 13664</td>
</tr>
<tr>
<td>Galactose</td>
<td>201</td>
<td>Char 1</td>
</tr>
<tr>
<td>Arabinose</td>
<td>165</td>
<td>Ash 8073</td>
</tr>
<tr>
<td>Xylose</td>
<td>414</td>
<td></td>
</tr>
<tr>
<td>Mannose</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>77247</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. The yields as mass/mass non-inert for the scenarios of SCWG plant integration (Paper IV)

<table>
<thead>
<tr>
<th></th>
<th>CHP-Inc-700</th>
<th>CHP-SS-700</th>
<th>H2-Inc-600</th>
<th>H2-Inc-700</th>
<th>H2-SS-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>2.495 x 10^{-3}</td>
<td>2.483 x 10^{-3}</td>
<td>2.979 x 10^{-3}</td>
<td>2.495 x 10^{-3}</td>
<td>2.483 x 10^{-3}</td>
</tr>
<tr>
<td>CO2</td>
<td>3.040 x 10^{-2}</td>
<td>3.437 x 10^{-2}</td>
<td>2.782 x 10^{-2}</td>
<td>3.040 x 10^{-2}</td>
<td>3.437 x 10^{-2}</td>
</tr>
<tr>
<td>CH4</td>
<td>7.748 x 10^{-3}</td>
<td>6.205 x 10^{-3}</td>
<td>4.746 x 10^{-3}</td>
<td>7.748 x 10^{-3}</td>
<td>6.205 x 10^{-3}</td>
</tr>
<tr>
<td>CO</td>
<td>1.344 x 10^{-4}</td>
<td>1.048 x 10^{-4}</td>
<td>1.239 x 10^{-4}</td>
<td>1.344 x 10^{-4}</td>
<td>1.048 x 10^{-4}</td>
</tr>
<tr>
<td>C2H6</td>
<td>2.282 x 10^{-3}</td>
<td>1.705 x 10^{-3}</td>
<td>9.769 x 10^{-4}</td>
<td>2.282 x 10^{-3}</td>
<td>1.705 x 10^{-3}</td>
</tr>
<tr>
<td>C2H4</td>
<td>1.495 x 10^{-4}</td>
<td>1.242 x 10^{-4}</td>
<td>2.251 x 10^{-4}</td>
<td>1.495 x 10^{-4}</td>
<td>1.242 x 10^{-4}</td>
</tr>
<tr>
<td>H2O</td>
<td>9.010 x 10^{-1}</td>
<td>8.983 x 10^{-1}</td>
<td>9.011 x 10^{-1}</td>
<td>9.010 x 10^{-1}</td>
<td>8.983 x 10^{-1}</td>
</tr>
<tr>
<td>char</td>
<td>9.011 x 10^{-3}</td>
<td>9.835 x 10^{-3}</td>
<td>1.454 x 10^{-2}</td>
<td>9.011 x 10^{-3}</td>
<td>9.835 x 10^{-3}</td>
</tr>
</tbody>
</table>

The process concepts were the same for all the scenarios: black liquor and recycled liquid fed to the reactor, brine and char separation in the reactor, and two-stage separation of products to hydrogen-rich and carbon dioxide-rich gases. Figure 5 shows the simulation model for the hydrogen production scenarios, valid also for the energy production scenarios except pressure swing adsorption (PSA) operation. The energy production scenarios utilized H2-rich gas for CHP production while the hydrogen production scenarios involved PSA to obtain pure hydrogen as the product and off-gas for energy recovery. The weak black liquor received from pulping unit (“BLFEED” stream) was not heated to supercritical temperature of water to prevent the salt deposition in pipelines. Instead, the weak black liquor and recycled liquid were fed to the reactor separately. When operating adiabatically, the temperature variation in the reactor was only around 15 °C. Temperature of the recycled liquid (“SCWRECyc” stream) was adjusted to obtain the set temperature in the reactor when
this stream was mixed with black liquor. The recycled liquid can be heated through flue gas due to high temperature. In addition, temperature of high-pressure separation was selected to maximize the heating value or hydrogen content of H₂-rich gas. Since the solubility of combustible gases decreases with temperature while vapor pressure of water increases, low temperature of 45 °C was selected for high-pressure phase separation for all scenarios. Regarding the heat integration, the specification of heat exchangers was defined as 20 °C temperature difference between hot inlet and cold outlet.

![Process simulation model for the hydrogen production scenarios (Paper IV)](image)

**Figure 5.** Process simulation model for the hydrogen production scenarios (Paper IV)

The equipment was sized based on the engineering design formulas (Sinnott, 2003), and the total capital investments were calculated based on the cost engineering principles (Brown, 2019). The costs were updated to the year 2018 by using chemical engineering plant cost indexes (CEPCI). Operating costs were also calculated based on the rules of thumbs (Brown, 2006). In addition, euro/dollar currency was assumed as 0.88 to convert the prices into euros. The reactor was scaled up proportional to the capacity and designed as two vertical vessels in parallel, with the same configuration as VERENA pilot plant to avoid plugging: inlet streams from the top and a dip-tube located at the center to transfer the gas product.
while separating the solid phase from downwards. The heat exchangers were designed as shell-and-tube type with the approximated heat transfer coefficients based on the phases of streams (Sinnott, 2003). The PSA design was simplified based on an investigation of hydrogen purification from a mixture similar to syngas (Ribeiro et al., 2008): four layered-bed columns with equal volumes of activated carbon and zeolite, the hydrogen recovery of 52 % and productivity of 59.9 mol H₂/kg adsorbent/day.

The profitability was evaluated based on net present value (NPV) and internal rate of return (IRR) for energy production scenarios and based on manufacturing cost of hydrogen for the hydrogen production scenarios. The project lifetime was assumed as twenty years with the linear depreciation model. The revenue involved the heating value in H₂-rich gas as CHP and the excess heat for the energy production scenarios while the revenue involved hydrogen in H₂ stream, off-gas used for CHP production and the excess heat. The excess heat occurred in the upstream of the “HPSEP” unit, as district heat due to low temperature. CHP process was assumed to generate energy as 30 % electricity and 70 % heat. With the electricity price of 75 €/MWh (Aalto University, 2019) and the district heat price of 60 €/MWh (European District Heating Price Series, 2016), the CHP price was 64.5 €/MWh as the price of energy associated with the heating value of black liquor and flue gas. The raw material cost was calculated as the cost of removing black liquor from the recovery boiler treatment as shown in Table 6. The pulping chemicals were assumed to be completely recovered by recycling the solid phase to the recovery boiler. Table 6 shows the cost of chemical loss for the purpose of sensitivity analysis. Paper IV specified other details of operating costs as well.

**Table 6.** The weak black liquor cost with the basis of 1 kg of weak black liquor (Paper IV)

<table>
<thead>
<tr>
<th>Commercial treatment operation</th>
<th>Remarks</th>
<th>Material and energy needed or produced</th>
<th>Contribution to the black liquor price (€/kg weak BL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation</td>
<td>Moisture down to 20 % In: 0.228 kg solid, 0.772 kg water Out: 0.217 kg solid, 0.054 kg water</td>
<td>325 kJ heat needed</td>
<td>-0.00542</td>
</tr>
<tr>
<td>Recovery boiler</td>
<td>In: 0.217 kg solid, 0.054 kg water 13.6 MJ/kg dry solid 88.5 % efficiency of steam gen.</td>
<td>1.26 kg air needed 89.6 kj preheating air 3.04 kj preheating BL 2.95 MJ</td>
<td>-0.01097 -0.001494 -0.00005063 0.04679</td>
</tr>
<tr>
<td>Chemical loss</td>
<td>Make-up to the digester 0.451 €/kg Na₂S 0.133 €/kg NaOH</td>
<td>0.037 kg Na₂S 0.012 kg NaOH</td>
<td>(0.01828) x loss fraction</td>
</tr>
<tr>
<td>Price of weak black liquor (€/kg weak BL)</td>
<td></td>
<td>0.02887 + (0.01828 x loss fraction)</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Partial wet oxidation of saw dust

Saw dust was exposed to hydrothermal liquefaction for selective production of sugars, furans, organic acids, bio-oil and lignin oligomers as presented in Paper V. The saw dust used in the experiments had the moisture content of 55.4 % by weight. The dry content involved 28.2 wt-% lignin and 70.6 wt-% polysaccharides consisted of glucose, mannose, arabinose, xylose and galactose.

The water:solid ratio was set to 11 by mixing 14 g of saw dust (55.4 % of which is moisture) with 62.5 g of water and placing this mixture to the autoclave reactor for the hydrothermal liquefaction experiments. Figure 6 shows the reactor configuration. Then, the reactor was heated to the reaction temperature followed by 30 minutes of isothermal reaction time. After the reaction time, the reactor was rapidly cooled to the room temperature to collect the product samples. Paper V provides more details about heating rate as well. The investigated conditions include 130-270 ºC, the presence or absence of 1.6 g/L sodium carbonate, and the presence or absence of oxygen with the partial pressure of 5 bars. Sodium carbonate was introduced to the mixture while oxygen was introduced after the heating stage and controlled through pressure of the system.

Figure 6. The reactor setup for the hydrothermal liquefaction experiments (Muddassar et al., 2015)
4. Results and Discussion

The research included experiments of hydrothermal conversion processes on black liquor as a challenging feedstock with sulphur and inorganic salts, and saw dust as a solid feedstock. The experimental results lead to process selection and a techno-economic assessment study. Afterwards, considering also the sustainability criteria, a hydrothermal biomass conversion is proposed together with a supply chain structure enabled by this type of conversion process.

4.1 Evaluation of PWO through Aqueous Electrolyte Modelling (Papers I & II)

Paper I evaluated PWO as an alternative treatment process for black liquor, with the target products of carboxylic acids or salts. Figure 7 shows the integration of PWO with a Kraft pulp mill. In addition, PWO would be applicable for non-wood mills as well.

Paper I investigated acid and salt recovery with respect to pH and the evaporation rate through a simplified aqueous speciation calculation. The carboxylates are in the carboxylic acid form at low pH around 2 and in ionic carboxylate form at high pH around 6 or higher. However, salt recovery requires an intensive evaporation due to dilute stream. Figure 8 shows the acid and salt recovery when evaporating 80 % of water before crystallization.
Figure 7. The integration of biorefinery process (top) and chemical production through PWO (bottom) (Paper I)

Figure 8. Acid and salt recovery after evaporating 80 % of water content (Paper I)
Figure 9 shows the process concept of the recovery based on evaporation and crystallization. However, this recovery process has issues regarding the implementation. The intensive evaporation is even not applicable for non-wood black liquor. High silica content limits the maximum solid concentration to around 50% regarding flowability. Moreover, the separation of each acid and salt would introduce another challenge as well. This process requires improved yields in PWO and effective separation after crystallization. Alternatively, Paper I suggested SCWG as the alternative process to avoid evaporation, with the target product of syngas.

![Figure 9. Process diagram for acid and salt recovery after PWO of BL (Paper I)](image)

From the phase equilibrium viewpoint, Paper I also highlighted the need of a new methodology for aqueous electrolyte modelling. Errors in Gibbs free energy calculation affects the chemical speciation and mass balances of a process when the concentrations are around saturation. In addition, obtaining the standard state specific heat of ions requires large amount of data and extrapolation to infinite dilution, introducing another inaccuracy to the calculation of total Gibbs free energy of a system. Paper II addressed these issues by proposing Gibbs free energy-based objective function for fitting the interaction parameters of activity coefficient models and fitting the standard state specific heat of ions with saturation data. The proposed objective function for fitting the interaction parameters provides more accurate speciation since this fitting method is more particularly
minimizing the errors at higher concentrations. In addition, the proposed method for fitting the ionic specific heats reduces the number of required data within a proper thermodynamic approach: the solubility data and activity coefficients at saturation at different temperatures are sufficient. Figure 10 shows the solubility estimates for sodium chloride-water binary system. For the Pitzer model, the system is defined as 1 kg water with sodium chloride in the amount higher than its solubility, arbitrary chosen as 8 mol, to determine the speciation through Gibbs free energy minimization. The proposed methodology improves the accuracy sharply for the empirical Bromley model. The proposed method improved the accuracy also for the advanced Pitzer model at high temperatures while providing fairly accurate results at low temperatures as well. In addition, Paper II shows the solubility estimates when the activity coefficient data is available up to a certain molality, instead of up to saturation. A thermodynamic validation was also illustrated in Paper II through standard state enthalpy of solution versus temperature. The future aspects of this study are to model multi-component systems with the proposed methodology and to include hydrated salts as well. This methodology would be useful when developing aqueous electrolyte models for biorefinery systems involving many compounds.

Figure 10. Solubility estimates for NaCl-water binary system (Paper II)
4.3 Evaluation of SCWG as the new alternative (Papers III & IV)

Paper III investigated the impacts of process conditions on the biomass decomposition mechanism and gas yields. The paper included experiments with model compounds of cellulose and lignin, i.e. SCWG of isoeugenol alone and sucrose alone, as well as black liquor. In addition, Paper III included also liquid analysis and discussions linked to the phenomena. Figure 11 shows the gasification efficiencies, cold gas efficiencies and gas yields for SCWG of black liquor. Temperature promotes the efficiencies and gas yields. As an exception, hydrogen yield decreases in Inconel reactor when temperature shifts from 600 ºC to 700 ºC. Regarding the catalytic impact of reactor wall, Inconel promotes the gasification reactions more intensively at high temperatures (at 600 ºC and 700 ºC), resulting in higher hydrogen and methane yields than stainless steel. The influence of alkali content was also described as accelerating the water-gas-shift reaction towards hydrogen and carbon dioxide generation, thus no carbon monoxide observed in gas product in case of SCWG of KBL.

Regarding the evaluation of SCWG as the alternative, syngas is considered for the purposes of hydrogen production or CHP production. The results show that the optimum conditions involve Inconel 625 reactor at 600 ºC and the same reactor at 700 ºC for hydrogen production and CHP, respectively, based on the hydrogen yield and cold gas efficiency. Nevertheless, despite lower gas yields than Inconel reactor, stainless steel reactor at 700 ºC is also worth considering for the feasibility study, due to remarkable difference in reactor material price.
Figure 11. The gas results of SCWG of KBL in stainless steel reactor (left) and Inconel 625 reactor (right): C/H/O GE representing carbon/hydrogen/oxygen gasification efficiency, $\eta_{(G)}$ representing cold gas efficiency (Paper III).

Paper IV investigated the feasibility of integrating SCWG to a Kraft pulp mill, based on the experimental results of Paper III. Figure 12 shows the input-output diagram of the scenarios: Inconel 625 reactor leads to higher hydrogen yield and energy than stainless steel reactor because of higher gas yields. Table 7 shows the total capital investments. The reactor material cost is the main difference between Inconel and stainless steel scenarios. Table 8 shows the operating costs, of which the main ones are black liquor cost and heat from flue gas to the recycling liquid. Table 9 shows the revenues.
Figure 12. Input-output diagrams of the integration scenarios (Paper IV)
Table 7. Investment costs in 2018 (Paper IV)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Fixed capital investment (M€)</th>
<th>Working capital (M€)</th>
<th>Total capital investment (M€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHP-Inc-700</td>
<td>58.9</td>
<td>5.2</td>
<td>64.1</td>
</tr>
<tr>
<td>CHP-SS-700</td>
<td>42.7</td>
<td>5.0</td>
<td>47.8</td>
</tr>
<tr>
<td>H2-Inc-600</td>
<td>57.0</td>
<td>4.9</td>
<td>61.9</td>
</tr>
<tr>
<td>H2-Inc-700</td>
<td>59.7</td>
<td>5.2</td>
<td>64.9</td>
</tr>
<tr>
<td>H2-SS-700</td>
<td>43.5</td>
<td>5.0</td>
<td>48.5</td>
</tr>
</tbody>
</table>

Table 8. Operating costs in M€/year in 2018 basis (Paper IV)

<table>
<thead>
<tr>
<th></th>
<th>CHP-Inc-700</th>
<th>CHP-SS-700</th>
<th>H2-Inc-600</th>
<th>H2-Inc-700</th>
<th>H2-SS-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor</td>
<td>23.09</td>
<td>23.09</td>
<td>23.09</td>
<td>23.09</td>
<td>23.09</td>
</tr>
<tr>
<td>Heat from flue gas</td>
<td>29.76</td>
<td>29.80</td>
<td>27.27</td>
<td>29.76</td>
<td>29.80</td>
</tr>
<tr>
<td>Electricity</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
</tr>
<tr>
<td>Insurance &amp; tax</td>
<td>1.77</td>
<td>1.28</td>
<td>1.71</td>
<td>1.79</td>
<td>1.28</td>
</tr>
<tr>
<td>Maintenance</td>
<td>3.54</td>
<td>2.57</td>
<td>3.42</td>
<td>3.58</td>
<td>2.57</td>
</tr>
<tr>
<td>Others</td>
<td>1.68</td>
<td>1.36</td>
<td>1.64</td>
<td>1.68</td>
<td>1.36</td>
</tr>
<tr>
<td>Total operating cost</td>
<td>61.8</td>
<td>60.0</td>
<td>59.1</td>
<td>61.8</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Table 9. Revenues in M€/year in the year 2018 (Paper IV)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>H₂-rich gas</th>
<th>H₂ Off-gas</th>
<th>Excess heat</th>
<th>Total Revenue</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHP-Inc-700</td>
<td>39.8</td>
<td>-</td>
<td>32.2</td>
<td>72.0</td>
</tr>
<tr>
<td>CHP-SS-700</td>
<td>34.4</td>
<td>-</td>
<td>31.6</td>
<td>66.0</td>
</tr>
<tr>
<td>H2-Inc-600</td>
<td>-</td>
<td>13.7</td>
<td>23.2</td>
<td>66.4</td>
</tr>
<tr>
<td>H2-Inc-700</td>
<td>-</td>
<td>5.2</td>
<td>32.1</td>
<td>69.5</td>
</tr>
<tr>
<td>H2-SS-700</td>
<td>-</td>
<td>7.2</td>
<td>26.8</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Figure 13 shows the profitability results as NPV for the energy production scenarios and as the manufacturing cost of hydrogen for the hydrogen production scenarios. For the energy production, Energy-Inconel-700 gives higher NPV and IRR (internal rate of return) despite higher capital investment. In contrast, stainless steel reactor provides cheaper production of hydrogen. Nevertheless, both Hydrogen-Inconel-600 and Hydrogen-SS-700 scenarios provide relatively cheaper hydrogen compared to the thermal processes for biomass conversion. Paper IV includes also sensitivity analysis for loss of pulping chemical and energy price, illustrating that Inconel reactor is more robust to these variations.
The profitability assessment includes two aspects to be validated: the gas yields in an industrial scale reactor and the calculations of profitability. Paper IV used the experimental data in the design by proportionally scaling up the reactor. Since surface-to-volume ratio influences the catalytic impact of reactor wall (Tuan Abdullah and Croiset, 2014), the gas yields should be verified in a pilot scale reactor as well. Nevertheless, the surface-to-volume ratio can be increased through special arrangements, e.g. multiple and coil-shaped dip-tubes in the reactor. In addition, the profitability assessment method includes simplifications and considered to have 30-50 % inaccuracy compared to the real values. Industrial implementation requires precise modeling for the simplified aspects of process design and updated market prices for the equipment and cost.
calculations. Nevertheless, this assessment is useful for the initial evaluation and comparing the process alternatives the detailed assessment.

SCWG can be an attractive treatment especially for non-wood mills. Non-wood black liquor can be concentrated only to around 50 % solid content for ensuring flowability, due to sharper increase in viscosity caused by high silica content, thus causing inefficiency in the recovery boiler. Since non-wood mills have currently no commercial treatment, non-wood black liquor cost can be counted as zero. However, this also means that the integration to a non-wood mill causes extra investment costs for the infrastructure of CHP production. As an advantage, non-wood black liquor has more hemicellulose and less lignin compared to KBL, i.e. less char and tar formation.

The main issues for industrial implementation include char formation and salt deposition causing plugging. Beside special reactor configuration enabling separation of solid phase, comprehensive investigations of conditions can help optimize the process in terms of gas yields and reducing char formation. Further investigations can include residence time and heterogeneous catalysts as well. Catalysts can improve the gas yields and/or reduce the reaction temperature to decrease the CHP need for the recycling SCW. For instance, PSI process operates at 400-450 ºC with Ru/C catalyst (Vogel, 2017). Bimetallic catalysts can also reduce char formation and improve gas yields. For example, Ni-Co/Mg-Al catalyst improved gas yield and reduced char formation through different components playing various roles in the reaction mechanism: Ni promoting decomposition and fragmentation of heavy organics, cobalt inhibiting repolymerization of phenolic fragments and Mg-Al support promoting depolymerization and fragmentation of organic constituents (Kang et al., 2017). As the other reason of plugging, salt deposition can also be addressed by a salt separator prior to the reactor, with a dip-tube or a rise-tube operating at slightly over critical temperature of water in a short residence time of few seconds (Boukis et al., 2017; Reimer et al., 2016). As the destiny of Sulphur includes hydrogen sulphide gas, separating Sulphur salts in advance can also provide Sulphur-free syngas, thus eliminating the need of gas cleaning when post-processing the syngas and the risk of catalyst poisoning in the SCWG reactor.
4.4 Partial wet oxidation of a solid feedstock (Paper V)

PWO can be the prior operation to the hydrothermal conversion of biomass even though Paper I concluded PWO not being promising for chemical production. Exothermic PWO phenomena can improve the energy efficiency of overall process by self-heating the feedstock. In addition, PWO facilitates the decomposition in the following hydrothermal conversion by lowering the molecular weight of lignin, dissolving solid feedstock and oxidizing Sulphur content. For instance, LignoForce process involves PWO of black liquor before acidification as an improvement to LignoBoost process: reducing the filtration resistance of lignin and providing Sulphur-free lignin product. Similarly, oxidizing Sulphur content in advance can provide Sulphur-free syngas and bio-oil when PWO is followed by SCWG or HTL. Furthermore, processing both liquid and solid feedstock would improve the techno-economic performance of a conversion plant. For instance, saw dust can be dissolved and partially wet oxidized in a single reactor.

Using PWO effectively in a conversion process requires knowledge about the impacts of process conditions on the decomposition phenomena and on the downstream composition. PWO conditions can be selected based on the energy optimization in an advanced process with multiple unit operations. Therefore, the criteria of selecting the PWO conditions should involve the balance among:

- the minimum loss of TOC to maintain the organic content for liquid feedstock
- the maximum TOC for solid feedstock, i.e. maximum dissolution with minimum decomposition
- the maximum temperature to reduce the heating need in further steps
- the minimum residence time to reduce the investment cost
- the minimum oxygen pressure to reduce the operating cost

The impacts of temperature, feedstock, catalyst and residence time were investigated for Kraft black liquor and wheat straw black liquor (Hassan, 2016; Muddassar et al., 2015). The optimum conditions were defined as 210 ºC and the oxygen partial pressure of 0.5 MPa with 10-20 minutes residence time.

Regarding solid feedstock, two-stage processing of saw dust was investigated for carboxylic acid production: alkaline pretreatment followed by PWO, investigating the impact of alkaline load in the
pretreatment on the carboxylic acid production in PWO operating at 210 °C and 0.5 MPa of oxygen partial pressure with 30 minutes residence time (Muddassar et al., 2014). The alkaline pretreatment dissolved saw dust with water-to-solid ratio of 10, heating the feedstock from 80 to 160 °C with 2 °C/min and 30 minutes of residence time at this temperature. Then, PWO is applied at 210 °C with the residence time of 30 minutes. Paper V investigated the impacts of oxygen and alkaline on PWO of saw dust in a single-stage operation, simultaneous dissolution and PWO. Figure 14 shows the influence of oxygen, alkaline and temperature on dissolution, TOC, pH and molecular weight for the water:solid ratio of 11 and 30 minutes residence time. TOC trends imply 210 °C as the optimum temperature with insignificant impact of alkaline and sharp promotion of oxygen. Even though the dissolution increases with temperature, decreasing TOC implies the decomposition of intermediates to carbon dioxide and water vapor in the presence of oxygen at temperatures higher than 210 °C.

Figure 14. The results for PWO of saw dust as a solid feedstock (Paper V)
4.5 The novel hydrothermal conversion of lignocellulosic biomass (Paper VI)

The selection of conversion process requires proper methodology based on the feedstocks, target products and feasibility assessments, as shown in Figure 15 (left). Then, Figure 15 (right) shows the scope of feedstock and products in Paper VI. Considering the comparison of conversion process types, hydrothermal processes are more suitable for biomass. For instance, SCWG is preferred to thermal gasification to produce syngas. Similarly, HTL is preferred to pyrolysis to produce bio-oil. In addition, lignin is a valuable material that can be recovered through quite simple operation. The products of lignin, syngas and bio-oil have usage in various sectors. The feedstock of the conversion process can include waste or by-products from various lignocellulosic biomass sectors, e.g. agriculture, forestry, pulp and paper industry.

Figure 16 shows the novel hydrothermal process producing lignin, syngas and bio-oil. PWO heats the feedstock and dissolve solid streams. Some portion of PWO downstream goes to lignin recovery through acidification. For alkaline lignocellulosic biomass, e.g. black liquor, lignin precipitates when pH is down to 9-10. The residual liquid of acidification and the other portion of PWO downstream goes through the reactor for bio-oil or syngas production. Multiple reactors in parallel enables simultaneous production of syngas and bio-oil as well. This process can operate flexibly based on the market demand on the products by adjusting the portion going through acidification and the reactor conditions. Based on the product demand, this conversion process operates in a flexible way by adjusting the flow rates and conditions in the units. The proportion to lignin recovery section can be adjusted based on the lignin demand. In the separation section, temperature of separators can be set in accordance with the desired use of syngas and solubility of gases based on the plant-wide optimization. Table 10 gives the process condition ranges.
Figure 15. The process design methodology (top) and the scope overview (bottom)

Figure 16. The proposed biomass conversion process for sectoral integration (Paper VI)
Table 10. Process conditions of the proposed conversion process illustrated in Figure 16 (Paper VI)

<table>
<thead>
<tr>
<th>The unit</th>
<th>The conditions</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWO</td>
<td>T: 170-240 °C</td>
<td>Self-heating of the feedstock</td>
</tr>
<tr>
<td></td>
<td>P_{OC}: 0.5-1 MPa</td>
<td>Dissolution of solids</td>
</tr>
<tr>
<td></td>
<td>t: 10-20 min.</td>
<td>Oxidizing Sulphur content</td>
</tr>
<tr>
<td>Acidification</td>
<td>T: 80 °C P: 1 atm</td>
<td>Lignin precipitation at pH 9-10</td>
</tr>
<tr>
<td>The conversion reactor</td>
<td>T: 600-700 °C P: ≥25 MPa</td>
<td>SCWG</td>
</tr>
<tr>
<td></td>
<td>t: 1-5 min.</td>
<td></td>
</tr>
<tr>
<td>The conversion reactor</td>
<td>T: 250-350 °C P: 4-22 MPa</td>
<td>HTL</td>
</tr>
<tr>
<td></td>
<td>t: 1-12 min.</td>
<td></td>
</tr>
<tr>
<td>HP G/L Separator</td>
<td>T: 45-250 °C P: ≥25 MPa</td>
<td>Separation of H₂-rich gas in case of SCWG</td>
</tr>
<tr>
<td>LP G/L Separator</td>
<td>T: 45 °C P: 1 atm</td>
<td>Separation of CO₂-rich gas for SCWG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separation of bio-oil for HTL</td>
</tr>
</tbody>
</table>

The proposed process has techno-economic benefits compared to the hydrothermal processes. Since PWO heats the feedstock without external heat supply, energy efficiency is improved compared to HTL or SCWG alone. In addition, as a critical aspect, Sulphur-free products can be enabled by introducing all oxidized Sulphur to the reactor with the aid of prior PWO since no significant Sulphur reduction occurs at temperatures lower than 900 °C (Wrobel, 2000). This would result in cleaner usage of bio-oil and eliminating the gas-cleaning need for post-processing syngas. As another critical aspect for hydrothermal conversion, the proposed process reduces char and tar formation as well since PWO partly decompose the molecular structures into smaller fragments.

As the future aspects, developing the proposed conversion process needs more investigations:

- experimental verification of sulphur recovery in brine or aqueous downstream
- validating the complete recovery of char and brine from the reactor
- lignin properties versus process conditions in PWO and acidification
- data on product yields of PWO-SCWG and PWO-HTL with different feedstocks
- kinetic and equilibrium modeling of biomass decomposition in hydrothermal conditions
- processing lignocellulosic and other biomass types together in this process
4.6 Sectoral integration as a sustainable supply chain network (Paper VI)

The proposed conversion process in Figure 16 enables the features of sustainable supply chain network of biomass: multi-feed-multi-product, flexibility for adjusting products, and adaptability to the variations in feedstock. Consequently, Paper VI proposed sectoral integration shown in Figure 17. The sectoral integration is an enhanced version of the distributed-centralized structure: processing both solid and liquid biomass from various sectors, and flexible operation to adapt changes in market demand and feedstock availability. The network involves the steps of biomass pre-treatment at each source site, transport to the regional conversion process, the conversion process at each region, transport to the centralized upgrading plant, upgrading to final product and finally transport to the demand places. The pre-treatments convert wastes in source sites to suitable feedstock for regional conversion plants. As a result, this network integrates various sectors providing feedstock for the regional conversion plants, thus providing additional income for rural areas as well as improving the environmental performance of the involved sectors. The pre-treatment operations can involve physical-chemical and/or mechanical processes, such as removing inorganic salts through ion exchange to avoid salt deposition in the hydrothermal process and dewatering and/or grinding to reduce the transportation costs. Afterwards, each regional conversion process produces CHP regionally, intermediates to be valorized in the central plants and/or products for other applications. For example, the proposed conversion process in Figure 16 can be the regional conversion process in the sectoral integration network: producing syngas for either energy or further catalytic synthesis, lignin for other industrial sectors, and bio-oil to be upgraded in a centralized plant. Finally, the centralized plants produce the final products transferred to demand sites.
The sectoral integration potentially provides a sustainable biorefinery. From the environmental viewpoint, this network structure improves the environmental performance of various sectors simultaneously. From the economic viewpoint, the network provides more revenue through valorization of wastes and by-products. Furthermore, the sectoral
integration also provides social development in rural regions by integrating local farming people, engineers, scientists and other associated business management people through the pretreatments at biomass source sites. This would result in even distribution of population over the rural and urban areas, thus facilitating the distribution of social services as well. In addition, this concept can potentially change the energy policy from central power plants for large areas to self-sufficient smaller regions in terms of energy when supported also with wind and solar energy. Furthermore, the potential implementation of the sectoral integration would provide independence with respect to energy to the countries with biomass activities. Especially, agricultural countries can fulfil energy and food need simultaneously, thus securing the most critical two sectors (Demirbas, 2009).

Developing sectoral integration network involves the aspects including:
- techno-economic analysis of the proposed hydrothermal process
- developing other conversion processes with the desired features for other target products
- sectoral integration with various regional conversion processes
- a supply chain with the whole waste biomass including other biomass types

Figure 18 illustrates the connections among biomass conversion processes, sustainable biorefinery and socio-economic situation. Biomass conversion processes have critical importance for achieving the criteria of sustainable biorefinery. Further developments on biomass conversion processes should continue regarding the desired features for enabling sectoral integration. Efficient supply chain network with advanced conversion processes would enable wide product spectrum, processing ability of various wastes and enhanced profitability. These benefits will result in socio-economic impacts including additional revenue, reduced financial risk through multiple value creation mechanism, rural development and eliminating the dependency on fossil sources.
5. Conclusions

The importance of biomass conversion has recently increased due to the environmental issues and depletion of fossil fuels. A sustainable biorefinery should provide fossil-independent production without compromising the critical needs including food and animal feed and with the ability to adapt changes in market demand and feedstock availability. From the societal and environmental viewpoints, 2nd generation biomass conversion processes are considered as potentially suitable solutions utilizing wastes and by-products even though these processes are economically uncompetitive compared to fossil-based productions and need techno-economic improvements. Therefore, the objectives of this research are defined as to develop a biomass conversion process and to determine the role of biomass conversion processes in a supply chain.

Biomass conversion processes are the heart of supply chain networks: influencing the economic and environmental performance of the whole chain as well as influencing the network design. The sustainability criteria direct the process development towards multi-feed-multi-product, flexible processes and assessments to the whole supply chain. The proposed conversion process improves the economic and environmental performance of multiple biomass sectors by utilizing wastes and by-products of these sectors. This enables a new supply chain structure introduced in this research, namely sectoral integration network. This network structure is an enhanced version of distributed-centralized network: additional revenue through waste valorization, more distributed financial benefits resulting in the development of rural areas, reduced financial risk through adapting the changes in market demand and feedstock availability.

Biomass conversion processes can be designed based on the target products and available feedstocks. Based on the properties of lignocellulosic biomass, hydrothermal processes are more efficient than
thermal and biological processes. This research proposed a new process producing lignin, syngas and bio-oil simultaneously from lignocellullosic biomass. The proposed process combines the benefits of partial wet oxidation, supercritical water gasification and hydrothermal liquefaction. This process is potentially beneficial for the post-processing syngas and bio-oil as well because of Sulphur-free products: avoiding catalyst poisoning, eliminating gas cleaning need for syngas and more environmentally-friendly usage of bio-oil.

The future aspects include the process development of the proposed conversion, developing other conversion processes fulfilling the sustainability criteria enabling sectoral integration, involving other biomass types and supply chain network design with sectoral integration structure.
References


American Institute of Chemical Engineers, 2005. DIPPR Project 801 - Full Version. DIPPR AIChe.


The environmental issues and depletion of fossil sources results in the increasing importance of renewable sources. As an abundant source, biomass has particular importance to achieve sustainable production of energy and chemicals. The societal and environmental aspects direct the biomass utilization towards waste or non-edible biomass, i.e. 2nd generation. On the other hand, 2nd generation biomass conversion requires advanced processes.

The objectives of this dissertation are to determine the role of biomass conversion processes in sustainable biorefinery and to develop a conversion process as the enabler of sustainable biorefinery. The criteria of sustainable biorefinery include fossil-independent production and flexibility to adapt the changes in market demand and feedstock availability. These criteria can be achieved with multi-feed-multi-product, flexible conversion processes. The conversion processes are to be selected in accordance with the target products and biomass feedstocks. Hydrothermal processes, using water as the reaction media, are suitable for biomass conversion regarding the high moisture and flexibility.